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BUCHANS

1996 - 1997 OVERVIEW

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SUMMARY

The 1997 experiments, in which phosphate was added to buckets of pit and Drainage Tunnel water, lead to the conclusion that phosphate can assist in particle formation and therefore remove zinc. The 1996 work, along with the completion of a MSc thesis, indicated that likely very little free zinc is present. The contaminant chemistry of Buchans waters is dominated by zinc-carbonate-bicarbonate formation. The resultant precipitation of zinc on particulates (mainly iron hydroxide) present in the water lead to removal of total zinc concentrations. Temperature and pH affect CO_2 degassing which in turn shift the carbonate-bicarbonate concentration ratios in all Buchans effluents. In 1997, the emphasis of the work was placed on a one-time application of phosphate to OEP. It was concluded that additions should be made, if at all, to the OWP at the Drainage Tunnel. The experiments indicated that phosphate performs as a flocculating agent. Particle formation and settling is affected by the hydrodynamic conditions in the pits, which appear to be more suitable in the OWP compared to the OEP. Insufficient data are available for scale up of phosphate application.

The mass balances of elements on site suggest that acid generation is taking place and that iron is recycled in both the OEP pit and the polishing ponds. Details suggesting acid generation were presented in an interim report submitted in July,1997. These findings should be verified. If there is a continuous generation of zinc in the system, then it follows that a one-time application of phosphate is inappropriate. The monitoring data summarized in this overview report suggests that flow regime in the polishing ponds has changed. More water is leaving the ponds 14 and 17 than is entering from OEP weir. The overview report highlights the new understanding of the zinc behaviour in the Buchans waters. It is imperative that this understanding is confirmed, before any further on-site work is undertaken.

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1.0 BACKGROUND: 1996 WORK

At the last owners' meeting, convened at the beginning of 1997, the results of the 1996 investigations of winter performance of the system were presented. In 1996, a 'new' understanding of the zinc removal process and the geochemistry of the Buchans ground water system became evident.

The 'old' understanding of zinc removal process and the polishing ponds, based on the previous years' work, has been summarized in Chapter 17 of a book which will be published in early 1998 by Springer: "Abatement of Geogenic Acidification in Mining Lakes", by Geller et al. Ed. (Appendix 1). The data collected prior to 1996 all agreed with the overall scientific understanding from the literature. Briefly:

Iron hydroxide surfaces facilitate the adsorption for zinc.

During the ice-free seasons, reduced iron present in groundwater enters the lower strata of the pits and is carried to the surface stratum where it oxidizes and hydrolyses as $Fe(OH)_3$.

Zinc along with iron hydroxide settle in the pit (quantified by sedimentation traps).

Further oxidation and particle settling take place in the polishing ponds. Biological removal of zinc by algal/moss growth in the ponds has also been verified; zinc carbonate is formed and biomass contains up to 40 % zinc (confirmed with Scanning Electron Microscopy). This zinc removal process is solidly supported by the older scientific literature. Non-performance in terms of zinc removal by the polishing ponds is explained by the absence of iron oxidation, and subsequent lack of particle formation required for zinc adsorption. This, combined with reduced growth of biomass (photosynthesis for zinc carbonate formation), explains the virtually negligible zinc removal during the winter.

The 1996 objectives were to address the winter performance as follows:

1 Define optimal conditions and location for the mechanism of zinc adsorption in the system (DT-OWP - OEP -Polishing Ponds).

2 Create growth conditions which provide adsorptive surfaces during the winter by stimulating phytoplankton growth.

3 Define the geochemistry of Lucky Strike - Valley seeps to clarify the understanding the dissolution/precipitation processes in effluents other than those from the OWP and OEP pits and ponds.

Many disciplines were utilized to achieve these objectives, namely geochemistry, inorganic chemistry, thermodynamics, hydrodynamics, particle science and biology. Given the diversity of disciplines, the 1996 final report resembled a tome of 153 pages. This report was essentially a data summary which required interpretation, as indicated in the summary (page vii, 1996 report).

1.1 1996 - 1997 Summary

The preliminary interpretations were presented during the 1997 owners' meeting. These findings radically changed the understanding of the 'apparent' zinc reductions in the OEP and the OWP and the overall functioning of the system. The nine main points are summarized with their consequences briefly below:

1 Zinc carbonate embedded between iron hydroxide particles: Little or no free zinc

In the last 3 years, a wealth of new information has come to light, through the use of a new powerful microscopic technology, regarding particle formation and its role as a cleansing mechanism in aquatic systems. Adsorption processes can now be investigated spatially. Amorphous solid phases can be differentiated from crystal-like forms, leading to new understandings of particle formation. Although the novel technology was not used for the investigation of the material in the sedimentation traps, SEM-EDX microscopy was used in the search for the location of the zinc in the iron hydroxide particles.

It was proposed that, through gaining knowledge regarding the form of zinc present on iron hydroxide particles, it would be possible to find means to improve the zinc removal. The SEM-EDX investigations did not find zinc particles at a magnification of 200 to 2000 times, but at 20,000 times, small (100 nm) particles containing up to 3 % zinc were identified, surrounding by big (1000 nm and larger) iron particles. The shape of the zinc particles suggest that they are likely zinc carbonate crystals forming inside the iron hydroxide particles. This is significant, since it suggests that there is little free zinc (the ion Zn^{2+}) in the Buchan system - it is, instead, present as zinc carbonate and is hence not very stable.

2 The total zinc concentration in OEP is diluted by fresh water input to the pit

The DT-OWP- OEP- Polishing Pond system was sampled for complete anion/cation balance for the first time. These data, together with recent flow information regarding the current configuration of the system, facilitated estimation of the complete mass balance of the water flows, using chloride (a conservative element in that it does not readily form precipitates). It became clear that fresh water input could account for the observed decreases in zinc concentrations in the OEP.

3 The mass balance of iron in the system indicates that iron is being recycled.

More iron is collecting each year in the sedimentation traps than can be accounted for by the ion concentrations in the ground water. A similar phenomenon appears to be occurring in the polishing ponds. Therefore, iron in recycling in OEP, and fewer new adsorption sites for zinc are being formed than first believed, based strictly on iron sedimentation rates.

4 Zinc removal from the water is independent of iron oxidation

An extensive series of iron oxidation experiments indicated that the oxidation and precipitation of iron as hydroxides in the effluents are not directly linked to observed reduction in total zinc concentrations in the Buchans waters.

5 Zinc carbonate forms as CO_2 degasses

The geochemical simulations of the formation of Valley seeps ground water and the results from the oxidation experiments indicate that degassing of CO_2 is the major driving force for the observed reductions of total zinc concentrations. With this process, the observed changes in pH and conductivity in all Buchan waters can be explained. It is highly These processes are likely highly related to zinc carbonate formation and its precipitation and removal out of the water column.

6 No phytoplankton or picoplankton in OEP

All other water bodies in the Buchan area showed some primary productivity, but nothing was found consistently in the OEP. It was suspected that the physical forces related to the stratification in the pit do not facilitate survival of the small cells. The hydrodynamics and light regime created by the upwelling groundwater and the formation, settling and recycling of iron hydroxides do not favour development of a phytoplankton population.

7 Phosphate fertilizer is captured by Mn and Fe

Field trial of additions of fertilizer to the polishing ponds indicated that phosphate precipitates relatively fast in the pond. It appears to associate with iron and manganese. This means that phosphate will end up in the sediment and its use as a fertilizer is limited by its natural recycling.

To establish sustained growth of the algal populations, appropriate N:P concentrations and ratios are required. Reliable data concerning nitrate concentrations could not be determined, while the source(s) of ammonia in the system is still not clear.

8 Phosphate as a particle formation agent

A MSc thesis on the nature of the particles in the sedimentation traps had been completed in 1996. It was found that, in the OWP, 50 % of the particles are 1 to 5 µm in size, while in the OEP, only 35 % of the particles are in this size category. Zinc is associated with all environmentally mobile fractions, based on a sequential extraction laboratory procedure. This also supports the contention that zinc is mainly present as a zinc carbonate. If this is indeed the case, then the replacement of carbonate with phosphate will be difficult.

Experiments were carried out in buckets with water collected from several locations. Additions were made to the waters representing molar ratios in such a way that the prevalent reactions and their rates could be deduced from the results. It became clear that the desired reactions replacing the carbonate with phosphate on the zinc are not likely taking place. Rather, the phosphate additions serve as flocculating agents. Details of these experiments, carried out by G. Neary on site, were summarized in the report, "Zinc Removal from Buchans Water" (July 20, 1997).

9 Acid generation and zinc loading

A one-time treatment of phosphate at the Drainage Tunnel appeared the most reasonable approach to addressing zinc removal. Such an approach to zinc removal is only justified if, indeed, the system is not continuously generating zinc, i.e., acid generation in the underground workings. The monitoring data collected to 1996 have been examined with respect to a mass balance on the zinc generated and zinc exported or discharged. It became evident that less zinc has remained in the system as precipitates than has left with the effluent. In other words, mobilized zinc is generated on an annual basis. If this is the case, then continuous, rather than a one-time, addition of phosphate would be required.

It was recommended that the monitoring data are utilized along with the atmospheric precipitation data to determine the sources of zinc . Phosphate application, designed to settle out zinc, has to target those locations in the system where most of the zinc originates, in order that zinc is retained at these locations. Furthermore, demonstration of precipitate formation resulting from the flocculation with phosphate has to be performed under dynamic conditions, as all of the experiments in the buckets represent static conditions. A scale-up experiment in the OWP is proposed for 1998 along with the geochemical analysis of the monitoring data to determine the acid generation rate and the associated zinc generation.

2.0 1997 MONITORING DATA

In Appendix 2, the monitoring data as of 1997 are summarized in the same fashion as provided in the 1996 Final Report. Brief statements about the monitoring data are given for 1997 below.

Figure 1a - 1b: River at Highway Bridge

The 1997 data reports the lowest concentrations of zinc detected since 1992 (Figure 1a). The range of pH fluctuations are not different from the ranges reported for the previous years (Figure 1b).

Figure 2a - 2b: River below Hydro Plant

The 1997 data contain the lowest records of zinc concentrations up to day 240 since 1992 (Figure 2a). For the remainder of the year, there was a dramatic increase in zinc concentrations up to 0.8 mg/L. The pH values not as variable as in previous years toward the end of the year (Figure 2b).

Figure 3a - 3b: Simms Brook

The zinc concentrations are not deviating from those reported prior to 1997 (Figure 3a). The 1997 pH values generally fall in the lower range of the annual seasonal averages (Figure 3b).

These data for the three monitoring stations suggest that 1997 was generally a wetter year, possibly diluting zinc concentrations passing through the drainage basins.

Figure 4a - 4b: Tailings Pond 1

Zinc concentration data for the middle of 1997 fluctuate more than in previous years (Figure 4a), but pH values are well in the mid range of pH fluctuations observed since 1992 (Figure 4b).

Figure 5a - 5b: Tailings Pond 2

Similar to TP1, larger fluctuations in zinc concentrations were observed in the middle of the year than observed in previous years. Towards the end of the year, the zinc concentrations were slightly below 2 mg/L, in contrast to 1996, when the concentrations had increased to about 4 mg/l at this time of year (Figure 5a). The 1997 pH values also show the opposite trend of lower pH towards the end of the year, compared to 1996 when the pH was generally higher towards the end of the year.

This pattern of zinc concentration confirms the previously identified source of zinc, the tailings beaches, via seasonal changes in water level. It is believed that, during 1996, construction of the weir in TP-2 produced water level increases and, hence, the increases in zinc.

Figure 6a - 6e: Drainage Tunnel

The zinc concentrations in 1997 showed the largest fluctuation ever reported throughout the year up to day 300. After day 300, a drastic decrease in zinc concentrations was noted. In fact, these are the lowest concentrations for this part of the year since 1992 (Figure 6a). The pH values in 1997 were generally lower than in previous years, with values sometimes even below 6, but no large fluctuations were recorded as noted for zinc (Figure 6b). Despite the large 1997 zinc concentration variation in the Drainage Tunnel, the average annual concentration was lower in 1997 compared to 1996, when the average increased compared to the previous year. However the average is associated with large

standard deviation as it was in 1995, thus the average concentrations since 1994 have to be considered as destabilized. This is likely a reflection of the Lucky Strike influence. The flows from the Drainage Tunnel in 1997 are generally lower than in the previous year by about 0.5 L/s, but the seasonal flow pattern is not the same, i.e, high or low flow periods do not correspond between the two years. Since the water level in the Lucky Strike has stabilized at its maximum elevation, the average flow in the Drainage tunnel has increased but is considerably less prone to fluctuations, which are generated in response to precipitation events (Figure 6e).

Figure 7a - 7c: Oriental West Pit

The OWP zinc concentrations should reflect a mixture of the Drainage Tunnel, the groundwater contribution from underground, and seasonally variable fresh water input. These variable inputs generated the observed large fluctuations noted in mid year (Figure 7a). The annual dilution of OWP by fresh water reaching the pit during spring run-off resulted in a low of about 2 mg/L, similar to 1992, the lowest dip reported in comparison to the previous years. The proposed equilibrium concentration around 15 mg/L was reached toward the end of the year. The process responsible for the apparent equilibrium concentration is not known. The pH values are very stable, as expected since all of the degassing will have taken place when the water reaches OWP through the Drainage Tunnel (Figure 7b). The average annual concentration of zinc continues to decrease, based on highly variable zinc concentrations (reflected in the large standard deviation), suggesting that the zinc concentration decrease in 1997 is greater than in previous years (Figure 7c).

Figure 8a - 8d: Oriental East Pit

The average annual zinc concentration continues to decrease, as noted in previous years (Figure 8a). The zinc concentration data for the pit outflow show that, during mid year, the lowest concentration of zinc ever leaving the pit since 1995 are recorded. However, by the

end of the year, the equilibrium concentration of around 15 mg/L is reached again (Figure 8b). The seasonal behaviour of the zinc concentrations in the OEP are plotted, omitting the higher values of 1995, for spring and winter, to demonstrate the shape of the seasonal changes in zinc, reflecting again the inverse of the pH curve (Figure 8c and Figure 8d).

Figure 9a-9c: Lucky Strike Glory Hole

The average annual concentration of zinc was still increasing in 1997, associated with a large standard deviation, nearly as large as calculated for 1991 and 1992 data (Figure 9a). With the exception of 1993, the seasonal behaviour of the zinc concentrations resembles that of the OWP, including the large decrease in concentration noted during spring run-off around day 120, followed by an increase over the remainder of the year (Figure 9b). The pH values for the Lucky Strike do not fluctuate very much (Figure 9c).

2.1 Flooded Pit Limnology

The profiles of temperature, pH, conductivity and dissolved oxygen concentrations have been periodically measured in the OWP, OEP and the Lucky Strike Glory Hole since 1989. In this period, some changes, in some cases major, to the hydrology have been induced. The surface waters of the OWP and OEP were joined by a culvert in fall, 1993. This resulted in a measurable surface flow from the OWP to the OEP. Upon joining the OWP and OEP, the OWP water level decreased, and the pH of this pit increased from pH 3.5 to above 5, where it has since remained. In August, 1994, all Drainage Tunnel water was directed to OWP.

Recent trends in the limnological profiles are examined below in light of general expected trends as well as these changes.

Figure 10: Lucky Strike (LS) Glory Hole

The limnological profiles of LS have been measured twice (September 27, 1996 and October 23, 1997). These measurements, presented in Figure 10, were collected after flooding of the LS Glory Hole was completed in 1995.

Temperature: Temperature measurements in September 1996 indicate that the LS was still stratified at this time, with a warmer, circulating layer of water about 12 m thick (epilimnion), overlying a cooler layer (hypolimnion) which was likely not circulating.

Temperature measurements in October 1997 indicate that the pit water had cooled to about 6° C, and may even have been turning over (whole pit mixing) at this time. Unfortunately, representative temperature data could not be collected to depths below 14 m, due to insufficient temperature probe cord length.

pH: The pH profile was measured at 1 m intervals in 1996, and at three depths in 1997. The pH of the LS appears to be stable with both depth and time over the last year.

Conductivity: In 1996, the conductivity was relatively constant between the surface and 13 m in the epilimnion. Below this depth, in the hypolimnion, the conductivity increased with depth, but sharply declined between 30 and 33 m. These last four measurements may be due to the probe sitting on/in the pit sediments. These 1996 measurements support the observation, drawn from the temperature profile, that the pit was stratified in September 1996.

In 1997, only a slight increase in conductivity was measured with increasing depth. This suggests that the pit had nearly completed mixing during fall turnover. However, pit water had not completely mixed with surface water.

Dissolved Oxygen: In 1996, the dissolved oxygen concentration in the epilimnion was relatively high (10 mg/L), but dissolved oxygen concentrations decreased with depth in the

hypolimnion to as little as 2.5 mg/L. The LS dissolved oxygen profile measured in October 1997 indicates that oxygen consumption was still occurring in the deeper portion of the pit in 1997. However, the decline in dissolved oxygen concentrations at depth is less steep in 1997, compared to 1996, likely due to greater mixing during fall turn-over in 1997.

Summary: Based on limnological data collected in September, 1996 and October, 1997, the Lucky Strike Glory Hole appears to thermally stratify during the ice free season, creating a circulating (mixing), oxygenated epilimnion in the top 13 m of the flooded Glory Hole. Below this, it appears that a more stagnant hypolimnion establishes during the ice-free season. Oxygen appears to be consumed in this lower half of the pit during the ice-free season.

Whether ice-free season stratification, spring and fall mixing (turnover) and oxygen consumption by pit water continues needs to be verified by repetition of measurements in all four seasons in 1998 and thereafter.

Figure 11: Oriental West Pit

Prior to joining OWP and OEP by a culvert in fall, 1993, the OWP water column consisted of low pH (3.5) clear water with virtually no suspended solids. The water column did not thermally stratify, due to good light penetration. Light attenuation was minor, and much of the pit bottom was visible from the surface (approximately 6 m visibility).

Following connection of the two pits, the water level in the OWP dropped, drawing in neutral pH, high iron solutions from the surrounding formations. The pH of OWP has remained nearly neutral since, but the pit water column continues to contain suspended iron particles, and water clarity continues to be low (< 1 m visibility).

In Figure 11, the September 27, 1992 data are presented, a sampling time prior to connection of the OWP and OEP. The following 12 sets of measurements were all performed following joining of the two pits by a culvert.

Temperature: On September 27, 1992, the temperature profile data shows that temperature did not change with depth, indicating that the pit was not stratified during the ice-free season. During measurements taken on later dates during summer or early fall, the pit water temperature was typically higher in the top 3 m, declining to a lower temperature in the lower portion of the pit. These data indicate that the pit stratified during the ice free season. Measurements taken in late fall (October, 1995 and October, 1997) show that the surface 3 m of water cooled, and no temperature gradient was measured.

Whether the pit turns over in early winter and freely mixes cannot be determined from the data collected to date. Limnological measurements in November and December prior to ice formation would help confirm seasonal water mixing patterns. Unfortunately those are not possible due to the ice conditions.

pH: Following joining of OWP and OEP with a culvert, the pH increased from 3.5 to neutral pH. The pH profile of OWP has remained relatively constant with time and depth on all measuring dates since.

Conductivity: Following joining of OWP and OEP, the conductivity typically increased with depth in the hypolimnion during the ice-free season when the pit is stratified. The lower conductivity in the epilimnion is maintained by constant input of Drainage Tunnel water which commenced in August, 1994. Conductivity in the upper 3 m in the epilimnion is constant with depth due to Drainage Tunnel inflow and wind-driven mixing. Below 3 m, conductivities are higher in the hypolimnion, likely due to higher conductivity ground water entering the pit at depth.

Most conductivity profiles show moderate variation with depth, except for data collected on October 11, 1995. On this date, conductivity was anomalously high in the hypolimnion, compared to previous profile measurements, most notably the profile measured earlier that year in July.

Dissolved Oxygen: Dissolved oxygen present in water bodies such as LS, OWP and OEP enters these solutions by diffusion from the atmosphere in the surface water, or as dissolved oxygen entrained in surface water flowing into the pits. Groundwater typically low in oxygen.

Dissolved oxygen in the surface water is distributed throughout the water column in periods when the entire pit is mixing due to wind driven circulation or in the mixing zone of oxygenated inflow and the pit surface water. Pit mixing can occur throughout the ice-free season in unstratified water bodies, such as was the case for OWP prior to its connection with OEP. Mixing can also occur in spring and fall, when there is no temperature gradient, in water bodies which are otherwise thermally stratified in the warmer months of the ice free season.

The OWP dissolved oxygen profile measured on September 27, 1992, prior to joining OWP and OEP, showed little variation with depth. This indicates that the whole pit volume was being mixed and separation in layers by thermal stratification was not occurring.

All dissolved oxygen profiles measured in OWP since September, 1992 indicate that mixing of the pit volume was not occurring. Dissolved oxygen concentrations typically decreased with depth, and showed a sharp decline in the transition zone from the upper mixed layer (epilimnion) and the lower, stagnant layer (hypolimnion).

The last set of measurements taken in October, 1997 show the greatest penetration of dissolved oxygen concentrations to depth in OWP, compared to other sampling dates. High dissolved oxygen concentrations at a depth of 8 m could indicate two phenomenon.

First, the October 27, 1997 profile was measured on the latest date in the fall season, compared to previous measurements. The elevated dissolved oxygen concentrations at depth could indicate that the pit's epilimnion, or stratum of circulating water, has penetrated to 8 m due to cooling of the water column and break-down of thermal stratification.

A second possible cause of relatively high dissolved oxygen at depth in October 1997 compared to previous dates is the gradual erosion since 1993 of the hypolimnion by continuous inflow of oxygenated Drainage Tunnel water. Again, until it can be confirmed that the entire OWP water column undergoes mixing in late fall (after October each year), it cannot be ascertained which process caused the elevated dissolved oxygen concentrations at depth in October, 1997.

Figure 12: Oriental East Pit

Since flooding of the OEP in 1987, a consistent discharge of water from the OEP of about 10 L/s has been measured. As described above, a culvert was installed in Fall, 1993 between OEP and OWP, and Drainage Tunnel water was directed to OWP in 1994. Since then, flow from OEP doubled, to about 20 L/s. The inflow from OWP to OEP can be expected to change the surface water characteristics from the period prior to connected of the pits. Whether this has affected the overall limnology of OEP is examined below.

Temperature: Temperature profiles measured in OEP clearly indicate that, during the ice-free season, the pit water column consists of a mixing epilimnion, about 3 m thick, and a hypolimnion, up to about 23 m deep at the deepest point. The profiles indicate that the hypolimnion has three distinct zones; the upper hypolimnion (3 m to 12 m), characterized by relative constant temperature with depth; the middle hypolimnion (13 m to 17 m), characterized by elevated and variable temperatures with depth and time of measurement; and a lower hypolimnion (18 m to 25 m), characterized by relative constant temperature with depth and time of measurement, similar in temperature to the depth between 5 and 12 m.

pH: The pH profiles measured in OEP have remained remarkable constant, at near neutral values, over the period of measurements (1992 to 1997). The pH slightly declines with depth over its profile.

Conductivity: Conductivity values have been variable both with depth and time of sampling over the measurement period. Typically, the conductivity is lower in the epilimnion, sharply increasing with depth at the epilimnion-hypolimnion transition depth, then gradually increasing with depth to about 20 m. Below 20 m, there is some indication that conductivity again decreases.

The higher conductivities in the middle hypolimnion could indicate that the warmer groundwater inflow with a higher conductivity, and may be connected with the underground mine workings. However, there is not a tight corresponding increase in conductivity at the same depths as temperature increases, and the relationship is overall weak.

Dissolved Oxygen: Like pH, dissolved oxygen concentration profiles have been remarkably consistent between sampling dates. The dissolved oxygen concentration in the epilimnion is consistently high, reflecting near-saturated concentrations expected for mixing surface waters. In the hypolimnion, the dissolved oxygen concentrations are always low.

Summary: Overall, it appears that the OEP remains stratified year round, due to the strong influence of the upward flow of anoxic, higher conductivity water originating from groundwater entering the pit.

2.2 Polishing Ponds

A brief discussion of the polishing ponds performance data is presented with the 1997 data, as was done for 1996 in Section 7 of the data summary report . For detailed text refer to the 1996 report. The data for 1997 are presented in Figures 13 to Figure 19. The zinc load leaving the polishing ponds in 1997 was higher during the winter month than in the previous year, although the loading from the OEP weir was lower than in the previous year. The loading of zinc within ponds 10 to 13 for the year 1997 suggests that a higher loading

is leaving pond 13 than entering pond 10 (Figure 14) during the winter months up to day 120. Thereafter, the trend changes and the ponds start removing zinc. For ponds 14 to 17, the same observation can be made with the new year, except that the difference in the zinc load leaving pond 17 and entering pond 14 is not as drastic as in the pond 13 to pond 10 system (Figure 15).

The data, when plotted for examination of zinc removal performance (Figure 16), suggests that during the winter months the system releases zinc, a trend not observed in previous years. The pH behaviour of the pond waters does not appear to reflect any changes, with the exception that the pH leaving the OEP weir has never been that low, and typically just slightly above pH 6 (Figure 17). However, the zinc concentrations for the pond system (Figure 18) in fact show lower concentrations for the final effluent in 1997, reaching values below 5 mg/L for the period between day 150 to day 240. A lower zinc concentration was also reported for OEP weir in 1997 of generally around 10 mg/L for the summer season. In Figure 19, the zinc concentrations in OEP weir and ponds 13 and 17 effluents are plotted for the season along with the concentration in the final effluent. A clear cut problem is evident; the final effluent zinc concentrations are lower in samples of water leaving the ponds compared to in final effluent samples collected downstream.

A brief comparison of the flows reported for the weir with the final effluent shows that, in 1996, essentially the same flow entering the system was measuring leaving the system. However, during 1997, although the average flow from the OEP is generally lower, the final effluents reports about 5L/s higher flow throughout the entire year.

It has to be concluded that the flow regime in the ponds has changed over the last year. The reason for this change in flow noted in 1997 is not clear but does explain the perception which is gained from zinc removal performance assessment. The ponds have changed flow regime and hence it appears that they release zinc.

2.3 Sedimentation Rates in OWP, OEP and Lucky Strike

The rate of sediment settling in OEP has been monitored since September, 1990. These measurements are collected in order to determine the mass of solids formed in the water column, containing the various element of concern including iron and zinc, which is settling out of the water column creating pit bottom sediments. This information is useful both during calculation of current contaminant mass balance and for examining approaches which would increase natural contaminant removal. All tables are given in Appendix 3.

2.3.1 Sedimentation Rates

OEP: Sedimentation traps have been installed at the centre of OEP at 4 m, 11 m and 20 depths, and at the outflow. Sedimentation rates in OEP centre at 20 m depth, expressed as g of solids settling per square metre per day, have ranged from 2.1 to 60 $g.m^{-2}.d^{-1}$. Excluding this maximum (possibly exaggerated due to sediment slumping), rates have ranged from 2.1 to 19 $g.m^{-2}.d^{-1}$. Sedimentation rates determined by traps positioned at 11 m range from 3.0 to 9.9 $g.m^{-2}.d^{-1}$, while shallow traps at 4 m have collected 3.9 to 5.9 $g.m^{-2}.d^{-1}$ (Table 1).

Overall, these data indicate that the sedimentation rates increase with depth of sampling by the traps. This indicates that more rapidly settleable particles are formed at depth in the OEP, and that rapidly settling particles are not forming only at the epilimnion-hypolimnion interface.

However, this does not exclude the possibility that small, slowly settling particles are forming mainly at the epilimnion-hypolimnion interface. As these slowly settle, they may be grouping into larger particles, which settle more rapidly. This would also account for higher sedimentation rates at depth.

Sedimentation rates determined near the outflow of OEP ranged from 0.62 to 4.6 $g.m^{-2}.d^{-1}$. This indicates that settleable particle formation is occurring not only in the main body of the OEP, but also in the outflow path.

OWP: Fewer measurements of sedimentation rates have been collected for OWP. The sedimentation rates range from 4.1 to 43 $g.m^{-2}.d^{-1}$. The value of 41 is likely accurate, since a second datum of 21 $g.m^{-2}.d^{-1}$ has also been recorded. It is somewhat surprising that these ranges are similar to OEP, since both a larger flow of groundwater enters OEP, and the OEP contains much higher dissolved iron concentrations at depth, compared to OWP. This may suggest that some factor common to both pits is limiting the rate of growth of particles to sizes which rapidly settle.

OWP typically contains more dissolved oxygen present to greater depths that OEP. Therefore, this would provide a larger volume of water in OWP where iron oxidation would proceed, compared to OEP, where oxygen is available only in the top 3 m. Conversely, the hypolimnion of OEP contains more dissolved ferrous iron and, therefore, a greater mass of iron ready to precipitate as iron hydroxide upon oxidation and hydrolysis.

It is unlikely, but not impossible, that these two phenomena roughly balance each other, such that similar sedimentation rates are occurring in the two pits. One alternative is that small, slowly settling particles aggregate into larger, more rapidly settling particles over similar vertical path length in both pits. This would imply that a significant fraction of iron hydroxide particles, formed in particular in the OEP, do not have enough time to settle and aggregate into large, rapidly settling particles. This fraction of small particles are carried with the pits' discharge.

The elevated turbidity in both pits, including the outflow water, suggests the latter alternative. The next opportunity for small particles to aggregate and settle is in the polishing ponds. During the ice-free season, the polishing ponds are very effective settling and filtration ponds for these solids, as was evident from the monitoring data.

Lucky Strike: Sedimentation rates in the Lucky Strike Glory Hole has been made for only one period (August 28, 1997 to October 9, 1997). Field personnel reported that negligible sediment collected in the two traps positioned at 5 m and 17. These traps should be re-sampled in the spring of 1998 to confirm this low rate. Similar reports were originally given for the OEP, suggesting that the observation of no sediment in Lucky Strike sedimentation traps were in error.

2.3.2 Cumulative Mass of Sediment Collecting in Pits

In Table 2, the mass of sediment (dry weight) which has collected in the OEP and OWP since sedimentation rate measurements began are calculated.

OEP: The annual mass of sediment settling to the bottom of OEP ranges from 40.5 t (1995) to 111.9 t (1992). This latter estimate appears to be high, in that the range excluding this year is 40.5 t to 56.2 t. Since the last sedimentation trap date was collected on October 22, 1997, the estimate for 1997 of 39.6 t is only a fraction of one year. The 1997 estimate is in line with the range of tonnages estimated for most other years.

There appears to be a slight decrease in the annual mass of solids settling with time. This is supported by diminishing iron and zinc concentrations measured in the OEP.

OWP: The annual mass of sediment settling to the bottom of the OWP appears to be increasing with time. The estimated masses are 4.3 t (1994), 10.1 t (1995), 19.2 t (1996) and 21.8 t (1997, part of year). The introduction of more dissolved oxygen by the Drainage Tunnel inflow may be responsible for more efficient iron oxidation and formation of rapidly settleable solids in the OWP. However, we are not sure if the amount of iron entering OWP in groundwater has been constant or increasing between 1994 and 1997. An increasing load of iron to the OWP could also account for the increasing mass of solids settling in the OWP. Without Fe concentrations determined for the system, the interpretation of the system's behaviour is not possible.

2.3.3 Particle Size Distributions in OWP, OEP and Drainage Tunnel

In 1992, the particles collected in OWP and OEP sedimentation traps were analysed granulometrically (Table 3). The results of this examination indicated that about half the particles sizes ranged from < 1 µm to 5 µm, while the remainder were between 5 and 25 µm in size. This suggests that relatively small particles make up the bulk of solids settling in the OWP and OEP.

In an effort to examine the particle sizes in OWP and Drainage Tunnel water, parallel samples (i.e., separate samples) were filtered through 0.1, 0.2, 0.45 and 0.8 µm pre-washed, pre-weighed filter papers. The dry weight of suspended solids collected on the filter papers were determined by subtraction the initial clean filter paper weight from the used filter paper. The results are presented in Table 4.

Using this procedure, small pore size filters should logically filter a similar or larger amount of solids than the larger pore size filter papers, as the small pore size should capture smaller particles plus all larger particles.

The results of these and other trials are generally inconclusive. For May 3, 1997 water samples of OWP and the Drainage Tunnel, the 0.1 µm filter papers contained less solids than larger pore size filter papers. Therefore, these results cannot be used.

The source of these inconsistencies probably lies in the small sample volume filtered (100 mL). For November 11, 1997 samples of OWP, larger volumes (250 mL) were filtered according to the same procedure described above. Both the 2 m and 7 m samples (but not the surface sample) yielded logical results, in that diminishing weights of solids were collected with increasing pore size. If these results are taken at face value, then they suggest that in water sampled at 2 m, most of the particles are smaller than 0.45 µm, while at 7 m, most of the particles are smaller than 0.8 µm. In other words, more particles are relatively small at a depth of 2 m, compared to the 7 m depth, where more particles are large. This concurs with the sedimentation rate results for OEP, where higher

sedimentation rates at depth were measured, compared to results recorded for sedimentation traps positioned at shallower depths. This further supports the hydrodynamic considerations which suggest particle aggregation or growth with depth (Interim Draft Report).

Appendix 1

Biological Polishing of Zinc in a Mine Waste Management Area

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Abstract

A comprehensive approach has been undertaken to develop a biologically-mediated treatment of mine effluent high in zinc. Using experts from a range of disciplines, the mine site was first assessed in terms of its hydrology, geochemistry, geology, biology, and water chemistry and, based on this assessment, a treatment strategy was developed. The treatment strategy was to employ biological polishing ponds to remove zinc. The approach was tested in a pilot scale study using polishing ponds connected in series. Based on five years' performance data, a full-scale polishing pond system was constructed. For the past two years, the pond has performed as predicted. It has removed 22% of the zinc from the waste water stream, when performance is annualized. Over the summer months, this section of the ponds has removed as much as 53% of the zinc. Winter performance is significantly lower, and efforts are being made to improve this performance.

Based on five years of performance data from the pilot-scale polishing ponds, the zinc removal process was shown to be self-sustaining. Furthermore, stable precipitates of this process (as originally hypothesized) have been found and identified. This was a critical finding supporting the self-sustaining nature of the process. And finally, some understanding of the precipitation mechanisms and the variables affecting them has been achieved. This understanding is essential for achieving further improvements in performance.

Biologically-mediated treatment technologies are more complex than traditional chemical treatment technologies, and conditions are not stable. They require a greater degree of understanding in order to function effectively. As illustrated here, this requires a multi-disciplinary approach coupled with an extensive analysis of data. However, once successfully established, biologically-mediated treatment processes offer a continuous, self-sustaining technology which will remove significant amounts of metal contaminants from dilute solutions in a cost-effective manner with low maintenance.

Introduction

Biologically-mediated processes have been used for at least 2,000 years to treat domestic sewage and agricultural effluent (Wang 1987). These natural water cleansing processes for both organics and inorganics take place not only in sewage and agricultural waste treatment systems, but also in natural systems such as wetlands, rivers, and lakes (Hamilton 1978). Effluents associated with mine waste areas are distinctly different from effluents produced by domestic and agricultural activities. Organic substances required to drive microbial activity are not present. As well, mine waste effluents are also characterized by low phosphorus levels, elevated concentrations of nitrogen compounds (remnants of blasting), high metal concentrations and often also extremes in pH. Natural treatment processes based on microbial mineralization of sewage or agricultural waste are therefore not directly applicable to mine effluents.

Organic matter can be supplied as easily degradable biomass and/or generated within the aquatic system though the productivity of species of phytoplankton and periphyton tolerant of conditions of mine effluent conditions (Kalin et al. 1989; Smith and Kalin 1991). Studies on passive (biological) treatment systems or constructed wetlands over the past decade indicate that metals are removed through absorption and precipitation of metal hydroxides (Kalin 1992). Under sulfate reducing conditions, Wieder (1992) found that iron became organically bound and also precipitated as carbonates or hydroxides. Such precipitates remove other metals from the water through adsorption, coprecipitation, and particulate formation (Kalin and Wheeler 1992a, b).

Biological polishing is a process for metal removal based on continuous algal growth on extensive surface (organic or inorganic) that absorb metals and trap metal precipitates via extensive colloid production (Kalin 1992; Kalin and Wheeler 1992a, b). In addition to biological factors causing precipitation and relegation of metals to the sediment, other physico-chemical factors affect the precipitate formation process, such as mechanisms affecting iron oxidation and reduction. All of these processes are essential to the design of treatment systems specific for a particular mine effluent.

Four zinc removal mechanisms were identified or hypothesized for this project. First, iron (III) hydroxides are precipitated as the groundwater enters the oxygenated flooded pit. A fraction of the dissolved zinc is coprecipitated or is adsorbed onto the surface of these precipitates. Second, suspended solids containing zinc adhere onto algal biomass surfaces. Third, dissolved zinc is adsorbed onto the algal cell walls. Fourth, a fraction of the zinc is precipitated as zinc carbonate on the algal mats which form in the discharge from the flooded pit. With this last mechanism, it was conjectured that the microenvironment surrounding the algae alters the solution properties (including pH), which leads to precipitation of zinc carbonate on algae surfaces.

This paper describes the approach used to reduce zinc concentrations in effluents from an abandoned mine. The treatment strategy employed biological polishing. In the waste water effluent, iron (III) hydroxides are precipitated in circum-neutral ground water discharging from old mine workings. These precipitates are removed from the water through adsorption on algal surfaces which grow attached to brush cuttings placed in the zinc polishing ponds. Although induction of particle formation is not brought about by microbially active sediments in this system, the performance of the biological components in the treatment ponds can be used to derive design criteria for biological polishing ponds in general.

Buchans, Newfoundland: A Case Study

The abandoned mine site is located close to the town of Buchans, in central Newfoundland, Canada (Figure 1). The waste management system consists of five mines (not shown), three pits, and two tailings ponds (Figure 2). The pits were mined by the gloryhole method, where ore was dropped from the mine seams to the bottom of the pit and hauled to the mill through underground workings. Zinc, gold, copper, and barium were mined from the Buchans site. At mine and mill closure, the pits and the underground workings were force flooded. Ground water flows into these gloryholes. The resultant overflow has significant concentrations of zinc. The overflow from all of the underground workings averages 20 L/s, contains 20 mg/L zinc and typically has a pH level of 6.5.

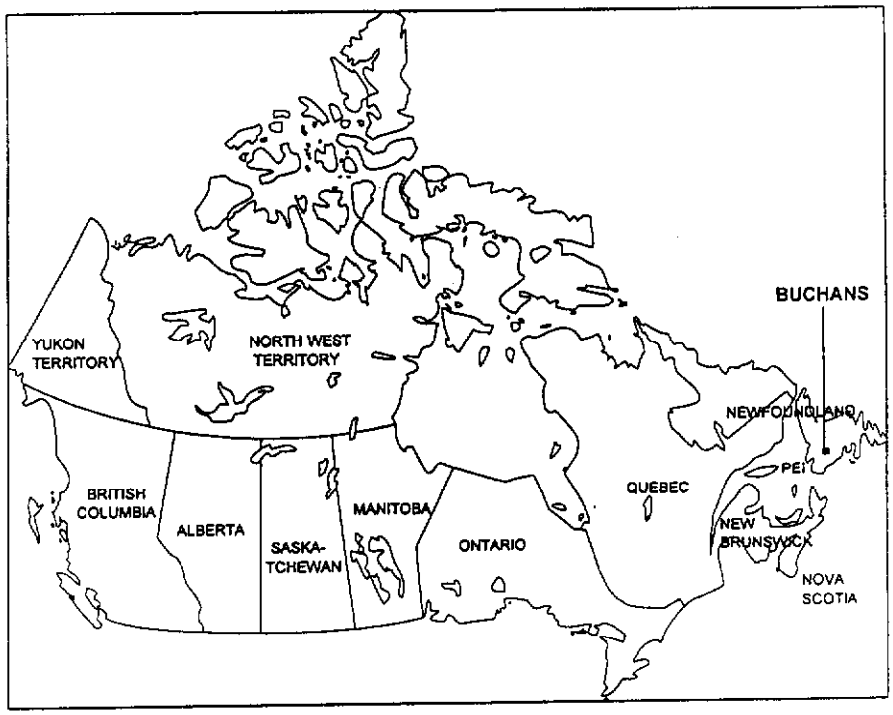


Figure 1: Map of Canada, showing the location of Buchans, Newfoundland.

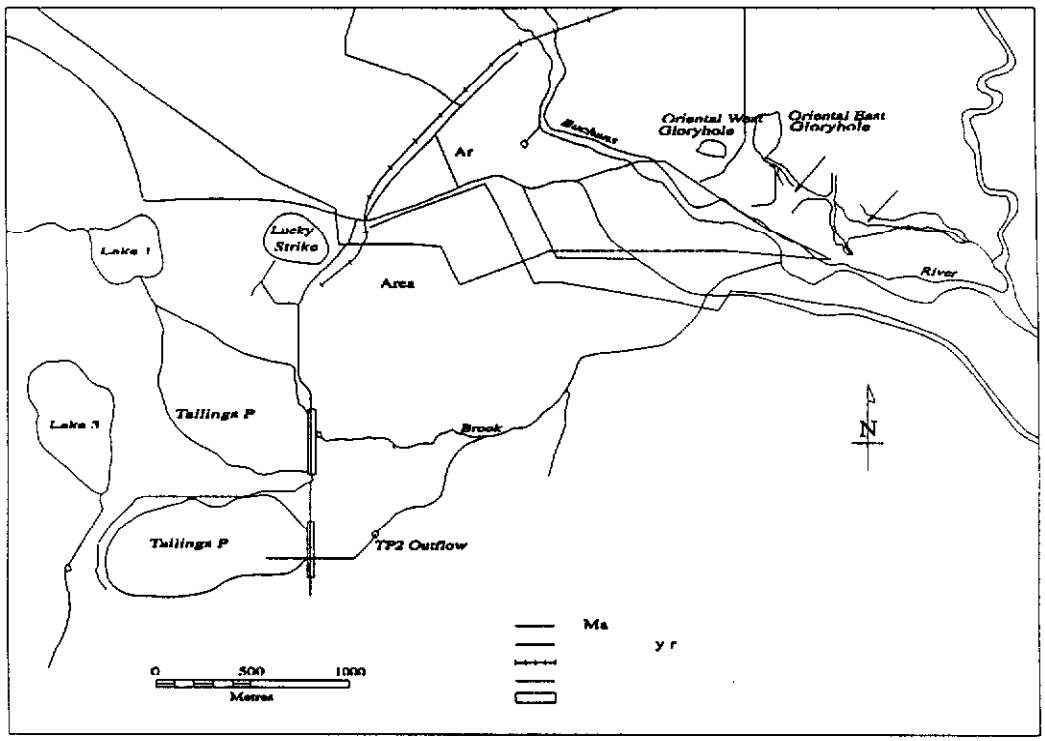


Figure 2: Map of the Buchans mine site, showing locations of gloryholes and waste water routes.

The methodological approach taken in finding a biologically-mediated solution consists of four stages.

Characterization of the mine waste site and assessment
Formulation of the treatment strategy
Pilot scale tests
Full scale treatment

As this was one of the first programs in which a biologically-mediated solution was sought for a site of this type, monitoring and assessment continues to be an ongoing process. This is absolutely essential, since each mine site environment has its own distinct characteristics which vary over the course of the year. As well, there is a significant amount of development work which must be carried out in effecting a successful biologically-mediated treatment program.

Characterization of the Mine Waste Site and Assessment

An extensive analysis of the mine site environment was first carried out. This began with a characterization of the hydrological and geochemical conditions to determine the source and mechanism of the continuous release of metal contaminant to the ground water. Water samples were analysed for metal and nutrient concentrations, pH, Eh, and temperature throughout the year. It was concluded that zinc was released via groundwater infiltration into the flooded underground workings. Next, taxonomic identification of the indigenous phytoplankton, periphyton, and picoplankton was carried out. Finally, particulate matter, both from the water column and sediment, was collected and analysed. A number of techniques were employed to analyse the particulates, including elemental analysis, sequential extraction, electron microscopy (SEM/EDX, i.e. secondary electron microscopy and energy dispersive X-ray analysis) and, in some cases, surface analysis (SIMS, i.e. secondary ion mass spectrometry). The large amounts of data collected were used for predicting the long term behaviour of the waste stream from the mine site.

This information was then combined with geochemical simulations, based on water chemistries, to determine optimal precipitation conditions. The literature was then reviewed based on the characterization of the metal concentrations and the algal species found. From these results, and particularly from our experience in developing treatment technologies, the natural processes which remove the metal contaminant (zinc) were defined. The exact removal mechanisms often are not proved at this stage, however a working hypothesis is arrived at. Based upon these removal mechanisms, the treatment strategy was developed which would enhance metal precipitation processes, and continuously (i.e. in a self-sustaining manner) remove contaminant, or at least inhibit its release.

The initial evaluation of the Buchans mine waste site had been carried out in 1988. The choice was to treat either the flooded pits directly, or the effluent flowing from them. The continuous upwelling of water in the flooded pits meant that establishing a stable sediment was not possible. Thus a treatment strategy using the ARUM (Acid Reduction Using Microbiology) process was therefore not optimal for this site. Instead, the decision was taken to employ biological polishing ponds for the pit effluents and enhance the zinc carbonate precipitation on the algal mats. Pilot scale testing was then the next step.

Description of Pilot Scale Biological Polishing Ponds

Previous work conducted on other systems resulted in metal removal rates for Ni, Zn, and As ranging from 0.1 to 3.8 $g/m^3/day$, iron removal rates from 0.04 to 39 $g/m^3/day$, and sulfate removal rates from 1.1 to 51 $g/m^3/day$ (Kalin et al. submitted). The relatively large ranges of removal rates were attributed to differences in retention times of the waste water in the systems, the surface area of microbially-active sediment in contact with the waste water, as well as the chemical characteristics of the waste waters passing through the systems.

The pilot scale system was constructed in 1989 (Figure 3) to develop optimal design criteria for biological polishing of acid mine drainage. Each of the six serial ponds had a surface area of 70 m^2 and a volume of 40 m^3. Alder branches were placed in each pond

to increase surface area (approximately 3.8 m^2/m^3) for algal growth. Flow through the pond was controlled to provide an overall residence time between 16 and 79 days.

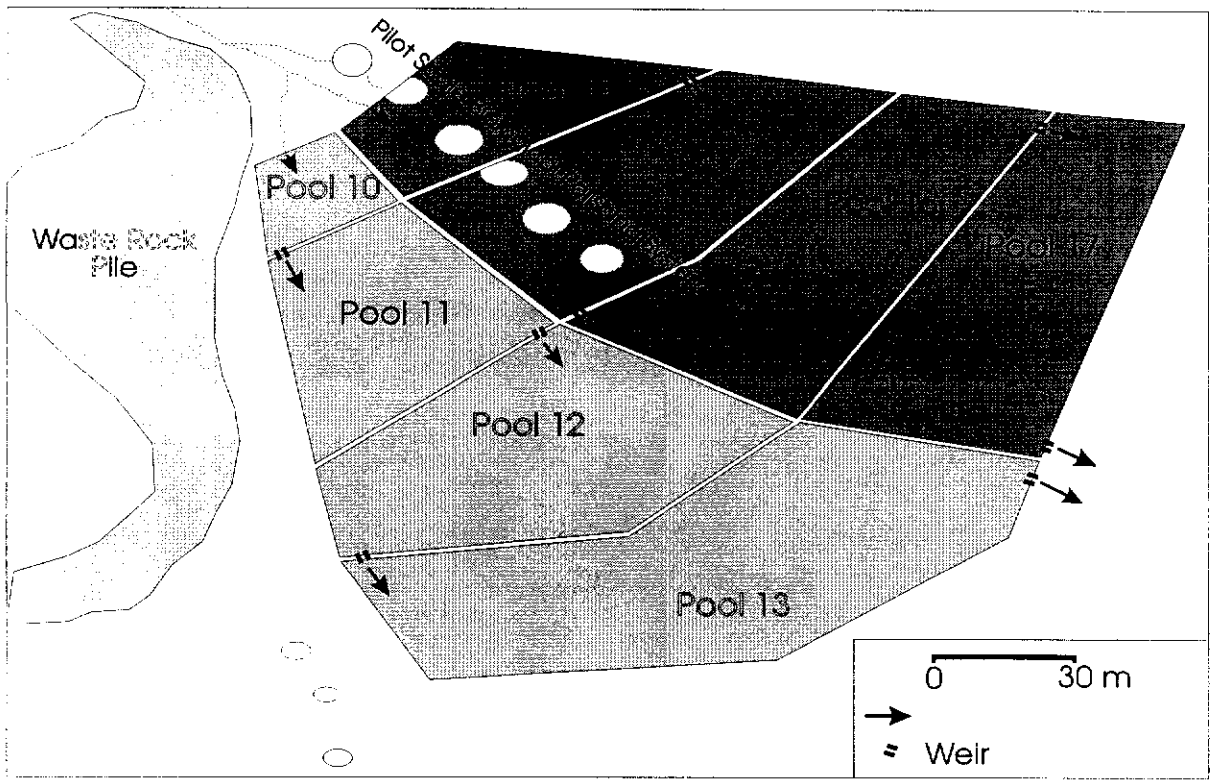


Figure 3: Layout of the pilot-scale and full scale biological polishing systems for removal of zinc in effluent discharging from flooded underground mine workings.

Data showing the performance of the series of six ponds are given in Figure 4. The zinc concentration decreases as the effluent passes through the pond system from an initial level of nearly 16 mg/L to 1.2 mg/L zinc (88% removal in water exiting the system). The amount of zinc remaining in each pond was determined in two ways; from the loss in the water, and from the concentration within the biomass lying on the alder branches. The greatest amount of zinc found in the algae or biomass coincided with the largest decrease in the zinc concentration in the pond water (pond 3; not shown).

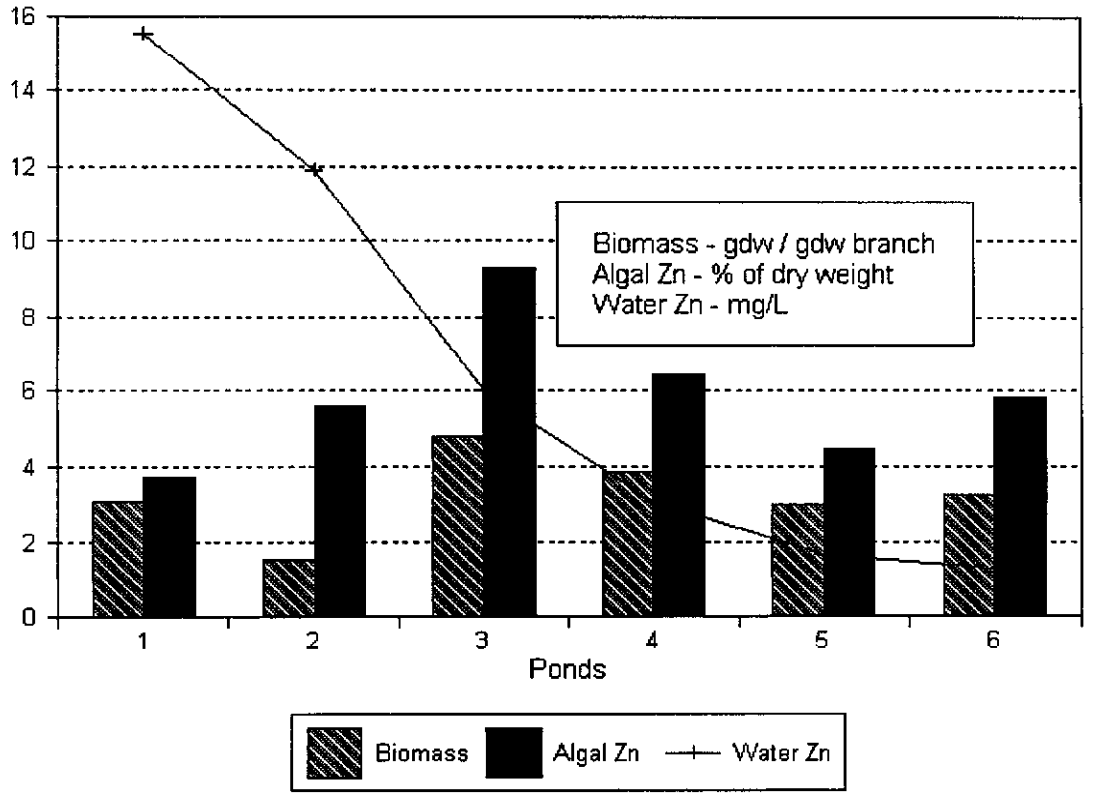


Figure 4: Zinc removal capacity and treatment parameters of the six pilot-scale ponds on August 25, 1990.

Figure 4 illustrates the two approaches which were used to evaluate the performance of the pilot polishing ponds. The first approach determines zinc removal in terms of the difference in zinc concentration in the pond water, flow rates, and residence times. The second approach assesses the algal growth and the concentration of zinc found in the algal biomass.

Using the physical approach (residence time), a linear regression analysis of the percent reduction in zinc concentration versus residence time of waste water passing through the pond system was performed using all pilot system data available for the period from 1989 to 1993, both winter and summer data (Kalin and Wheeler 1992b). From this analysis it was projected that a zinc concentration decrease of 2.2% per day of waste water residence

time could be expected in the full-scale system. It was observed that the zinc removal rate increased substantially over the summer months. From a regression analysis using 8 sets of data for summer months alone, it was projected that a zinc concentration decrease of 5.2% per day could be expected during summer months (Kalin 1992, Kalin and Wheeler 1992b).

Next, performance based strictly upon algal growth rates and algal zinc content was determined. The measure of performance is in terms of zinc removed per surface area of algae. Algal growth was quantified by suspending netting of a known surface area in the polishing pond and collecting the biomass at different intervals during the growing season (Kalin 1992, Kalin and Wheeler 1992a). Assuming an average growth period of 100 days in the summer, the growth rate of algae on the netting was determined to be 0.75 $g/m^2/d$. If the growth were averaged over the entire year, a growth rate of 0.20 $g/m^2/d$ would result. Analysis of the algae indicated that one kilogram (dry weight) of this biomass contained 34.7 g zinc.

The effect of fertilizer additions (Plant Products 10-52-10) on algal growth in the pond system was also determined. Addition of fertilizer resulted in growth rates two to three times those of the unfertilized algae. It was anticipated that these increased growth rates would result in increased zinc removal by the biological polishing ponds.

Using both approaches, there was no deterioration in the performance of the polishing ponds over the five year study period. If removal mechanisms only involved the ion exchange capacity of the polishing ponds, saturation effects would have been evident. In other words, continuous removal mechanisms were operative, although the mechanisms involved were not fully understood.

Scale-up Design to the Full-scale Treatment System

Based on the results from the pilot-scale tests, design criteria for a full-scale treatment system were developed. It was decided that two full scale systems would be constructed to operate in parallel. Each system would be comprised of four ponds in series (Figure 3).

Each full scale system would have a surface area of 13,100 m^2 and a capacity of 6,000 m^3. The design flow rate was 4.7 L/s, which would result in a residence time of 15 days. Subsequent changes in water flow at the mine site increased the actual flow rate to closer to 9 L/s. Using the full year pilot projection of 2.2% zinc concentration reduction per day of residence, a 32% reduction in zinc was expected. Using the summer reduction rate of 5.2% per residence day, it was estimated that 78% of the zinc should be removed.

Performance based strictly on algal growth rates and algal zinc content was examined for comparison to that based on percentage zinc removal-residence time above. By multiplying the amount of biomass produced per day by the zinc concentration associated with that growth, an estimate of the amount of zinc removed per day was obtained. The total surface area for periphyton growth was calculated from the estimated average surface area of a cutting of alder brush (including leaf area) and the number of brush cutting used. Using the conservative annualized growth rate and zinc concentration data, it was projected that in a scaled-up system with 51,000 m^2 of substrate surface area provided by alder brush, 1.1 kg of zinc would be removed per day by the periphytic algal population in a 6,000 m^3 full-scale biological treatment system (Table 1). This number would increase in summer to approximately 3.2 kg zinc/d zinc or greater if the fertilized growth data was used.

Table 1: Projected performance of polishing ponds 10 to 13 based on pilot-scale performance using algal growth rates and zinc concentration.

	Performance Data All year	Performance Data Summer	Units
Average Algal Growth Rate without Fertilizer (Netting, Branch data)	0.20	0.75	$g/m^2/d$
Zinc content (1994-1995 data)	35	35	g zinc/ kg dw algae
Surface Area in Pond System ($3\ m^2$ per brush cutting with leaves x 17,000 brush cuttings)	51,000	51,000	m^2
Algal Biomass Growth	33	92	kg/d
Estimated Zinc Removed by Periphyton	1.1	3.2	kg/d
Zinc Load, (4.7 L/s flow; 15 mg/L, 1994-1995 Avg [Zn] in OEP discharge)	6.1	6.1	kg/d
Estimated % Zinc Removal by Periphyton	18	53	%

Full Scale Biological Polishing Pond Performance

Construction of the first section of the full-scale system was completed in late fall, 1993. Alder brush was placed onto the ice-covered ponds in November, 1993. An average flow of 8.5 L/s passed through the system over the next year, which resulted in a calculated residence time of 8.2 days (Table 2). During the summer months, the average flow was 4.9 L/s, giving a calculated residence time of 14.2 days, close to the design specifications for residence time. During 1995, the second year of testing, the flows averaged 8.8 and 8.5 L/s for the year and summer, respectively. These final flows were higher than originally anticipated.

Despite the higher flows (and lower theoretical residence times), the performance of the scaled-up system was higher than predicted. The annual average of 31% and the summer

average of 66% zinc removal indicate that flow and residence time are not the only factors that control zinc removal. During the second year, the percent zinc removed was slightly lower (22% and 53% for annual and summer calculations), due to the much higher flow rates during the summer. However, the total amount of zinc removed during that summer was actually greater during the second year (4.7 vs. 3.5 kg/d).

Table 2: Actual performance of polishing ponds 10 to 13, 1994-1995.

	Performance Data All year	Performance Data Summer	Units
1st year: Flow In/Out	8.5	4.9	L/s
Load In	10.6	5.3	kg/d
Load Out	7.3	1.8	kg/d
Total removed	3.3	3.5	kg/d
Percent removed	31	66	%
2nd year: Flow In/Out	8.8	8.5	L/s
Load In	9.8	8.8	kg/d
Load Out	7.6	4.1	kg/d
Total removed	2.2	4.7	kg/d
Percent removed	22	53	%

Performance in the first year was very close to that predicted based on residence time. However, the flow into the system was considerably higher than the design criterion (8.5 L/s compared 4.7 L/s). This greater than predicted performance is attributed to adsorption onto the surfaces of the newly-placed alder cuttings. In the second year, the performance dropped to an overall 22% removal which is closer to the prediction based on year-round data (32% based on residence time and 18% based on algal growth). Considering only data for the second summer, actual removal rates (53%) closely matched those predicted based on algal growth (52.5%).

Discussion

Determining a process which is self-sustaining, proving the process with pilot scale testing, and then scaling up to a full scale system is not the end of the development of the biologically-mediated solution. Process optimisation continues, based upon finding and

understanding the mechanisms involved in removing the zinc.

One of the first steps in determining a suitable treatment strategy was defining the removal mechanisms involved. We postulated that the following four mechanisms may be involved. First, iron (III) hydroxides are precipitated as the groundwater enters the oxygenated flooded pit. A fraction of the dissolved zinc is coprecipitated or is adsorbed onto the surface of these precipitates. Second, suspended solids containing zinc adhere onto algal biomass surfaces. Third, dissolved zinc is adsorbed onto anion groups on the algal cell walls. And fourth, a fraction of the zinc is precipitated as zinc carbonate on the algal mats which grow in the discharge from the flooded pit. In this last mechanism, it was conjectured that the microenvironment surrounding the algae may be altering the solution properties (including the pH), which in turn leads to the precipitation of zinc carbonate in the vicinity of the algae.

Evidence for the first mechanism is found in the chemical analysis of material collected in sedimentation traps suspended in the flooded pit. Concentration of zinc ranged from 1.1 to 2.5% of sediment dry weight. In addition, SEM/EDX analysis carried out on the precipitates formed in the flooded pit displayed grains which were uniformly coated with what appeared to be precipitation products, having high Fe (40-70%), Si (15-30%) and significant amounts of zinc (approximately 3%). Iron precipitates which remained suspended and flowed into the polishing ponds could be removed by adhering to the periphyton growing in the ponds; the second zinc removal process.

Direct evidence for the second mechanism was obtained through studies of the metal co-precipitation associated with algal/moss growth in waste water at Buchans and other sites. These populations, because of the close interaction between precipitate and periphyton, have been termed periphyton-precipitate complexes (PPC). The periphyton populations found in the polishing ponds are mainly composed of green filamentous algae. In the absence of precipitates or suspended solids, they contain percentages of zinc of 1% or less. PPC growth rates were quantified in the six pilot scale polishing ponds in the Buchans waste water, using either an artificial substrate or alder branches. The artificial substrates, called "peritraps", consisted of an artificial netting structure which housed alder

branches. The PPC mass was cleaned off the nets and branches, dried, weighed, and analysed for elemental content. The percent content of likely compounds of the major elements are presented in Table 3. Loss on ignition can range from 25 to 42%, through the volatilization of organic and inorganic carbon as CO_2, hydroxides and water from hydrated compounds (Table 3). Other compounds accounting for the remaining 36% could include mainly sulfur and silicon compounds.

Table 3: Composition in periphyton-precipitate complexes (PPC) in percent of dry weight.

Taxa	Algae	$Fe(OH)_3$	$Zn(OH)_2$	$Mn(OH)_5$	$Al(OH)_3$	$CaCO_3$	Other
Microspora	18.7	21.4	12.7	3.6	3.5	4.1	36.3

The source of the hydroxides is, first, the flooded pit immediately upstream of the polishing ponds, and second, from further precipitates formed in the ponds themselves. Related work done on PPCs in other waste water bodies and at Buchans was carried out matching precipitate "growth rate" with the growth rate of the algal portion of the PPCs. The "growth rates" matched well. This suggests that the periphyton surfaces and associated polysaccharides exuded by them are providing a "sticky" surface which appears to remove not only precipitates from the water which have adsorbed zinc, but also some of the dissolved zinc (filtrable through 0.45 µm). This provides evidence for the third mechanism of zinc removal.

Evidence for the fourth mechanism was obtained from analysis of surfaces of algae/moss growing in the polishing ponds using a high resolution scanning electron microscope (SEM) and energy dispersive X-ray microanalysis (EDX) using a windowless detector which allowed quantifiable detection of light elements, including carbon and oxygen. Large precipitates were observed among the filamentous algae (Figure 5). The precipitates, which were several µm in size, were spheroidal in shape and clustered in large clumps between thin filaments of algae. Elemental image mapping showed that these precipitates were composed of zinc and carbon, with significant amounts of manganese. This provided strong evidence for zinc removal by precipitation as zinc carbonates.

Figure 5: Scanning electron microscope photograph of a leaf surface with filamentous algae and precipitates.

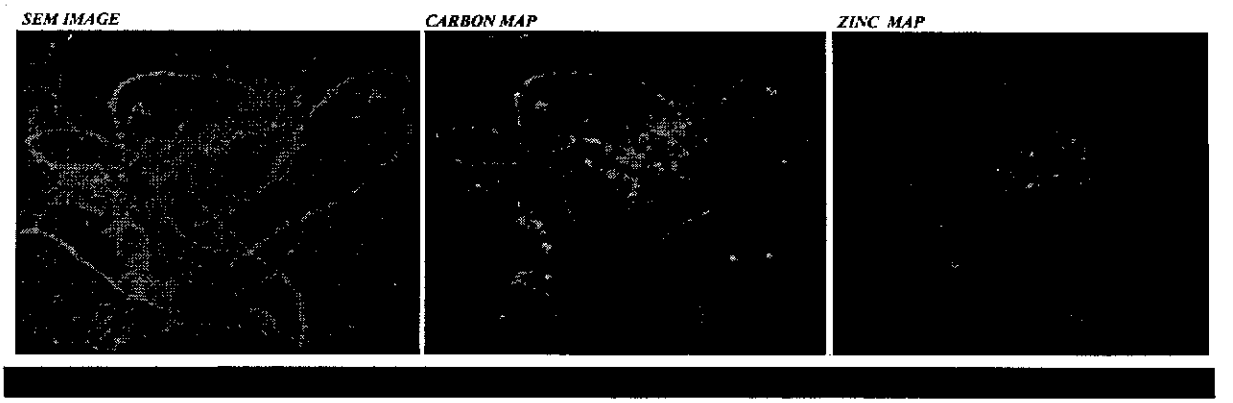
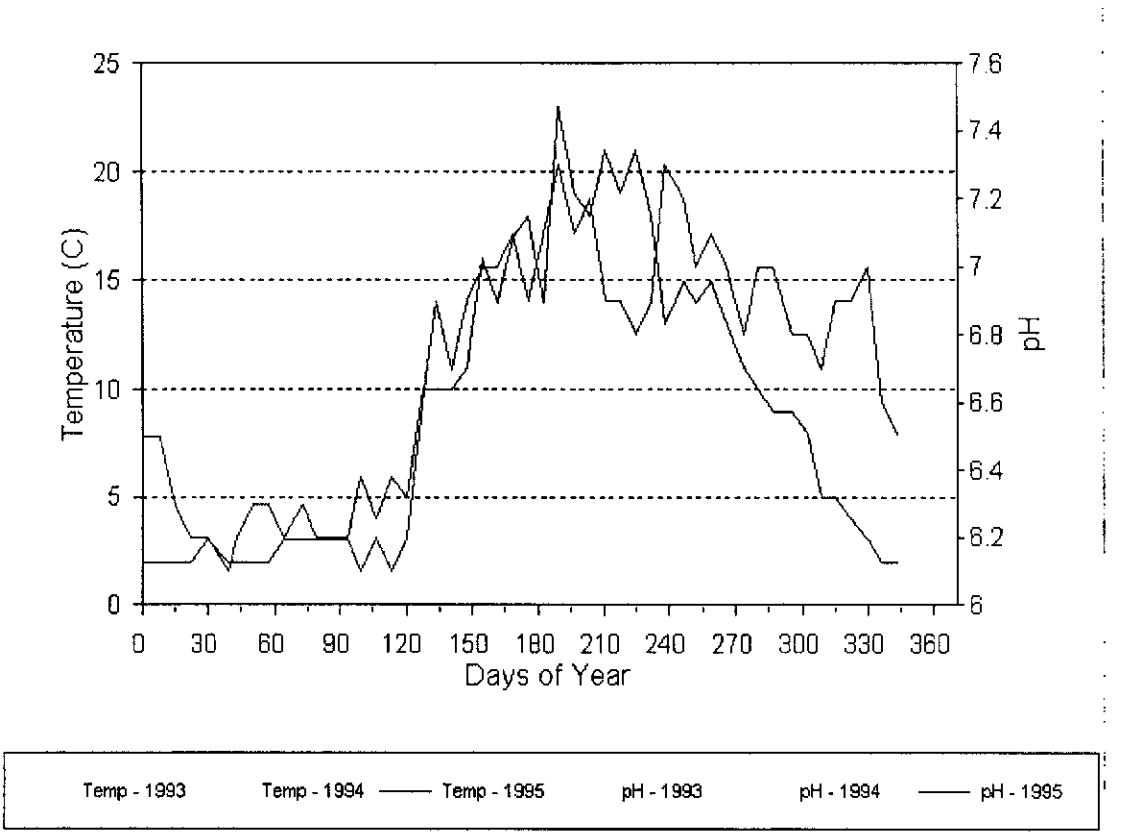


Figure 6: Temperature and pH changes recorded throughout the year at the outflow of the gloryhole.



The polishing pond performance during the summer was good. The winter removal rates were significantly lower. There are a number of factors which may account for this. The temperature and pH of the water flowing into the ponds changes significantly over the course of the year (Figure 6). The temperature increases from 3-5 °C during the winter to over 20 °C during the summer. The pH of this water increases from approximately 6.5 during the winter to approximately 7.2 during the summer.

A further factor which affects the metal precipitation conditions is the oxygen concentration in the water. During the winter, the aeration of the pit and the ponds is almost eliminated by the formation of ice on top of the ponds. The combination of the lower temperatures, pH levels, and concentrations of dissolved oxygen of the waters results in reduced iron hydroxide formation. Due to reduced algal growth rates, zinc carbonate precipitates on the periphyton is also reduced.

Zinc removal is affected not only by its coprecipitation (adsorption on iron hydroxide precipitates) but also by its adsorption and adhesion onto algal surfaces and extracellular polysaccharides. The increased effectiveness in zinc removal during the summer can also be ascribed to the growth of the algae, since algal surface areas for adsorption, filtration, and coprecipitation are constantly increasing. A decreased effectiveness during the winter may be the result of reduced pond volume in the winter due to ice formation.

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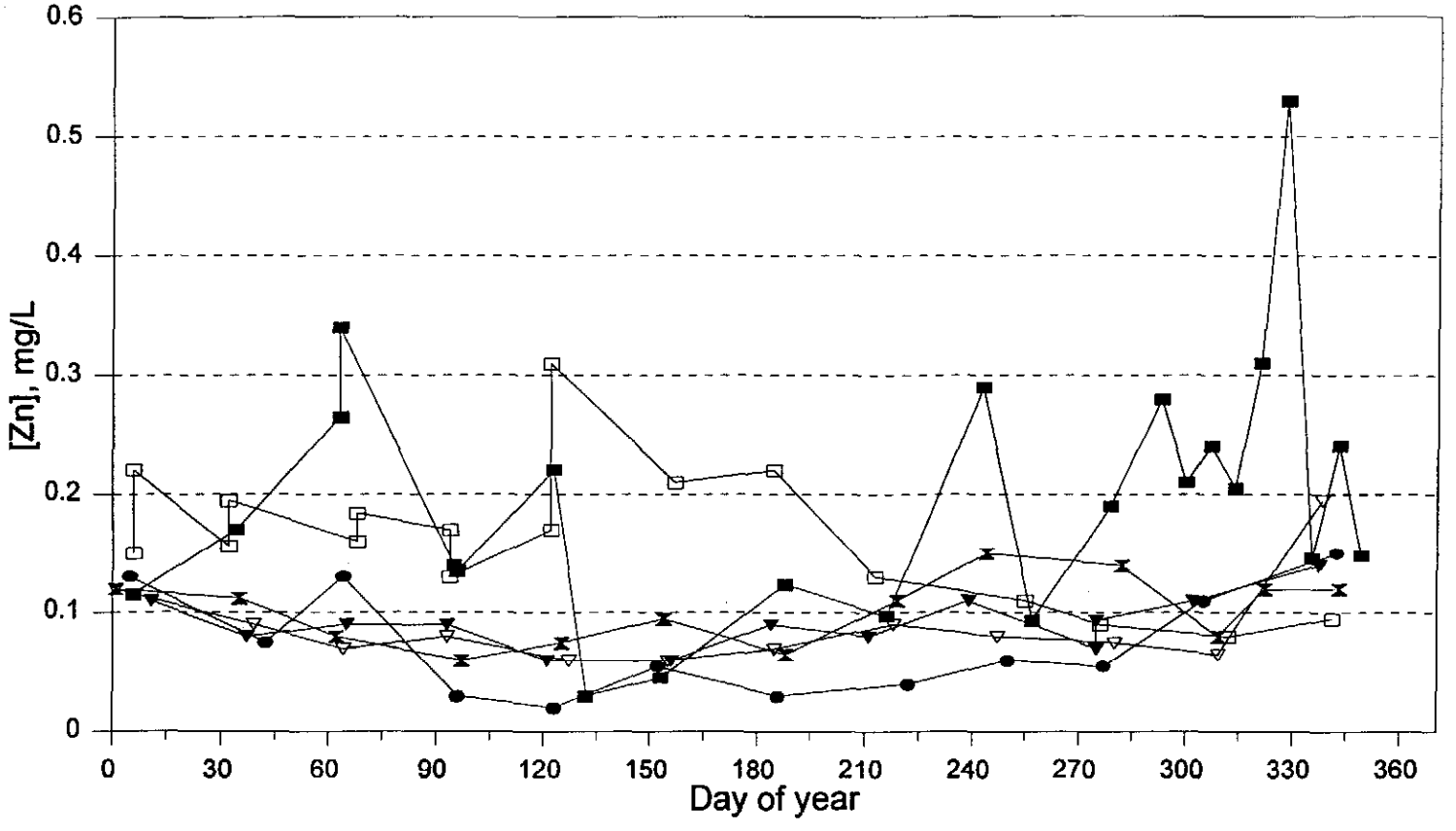
Fig. 1a: River at Highway Bridge

Zinc Concentration, 1992-1997



Appendix 2

Fig. 1b: River at Highway Bridge

pH, 1992-1997

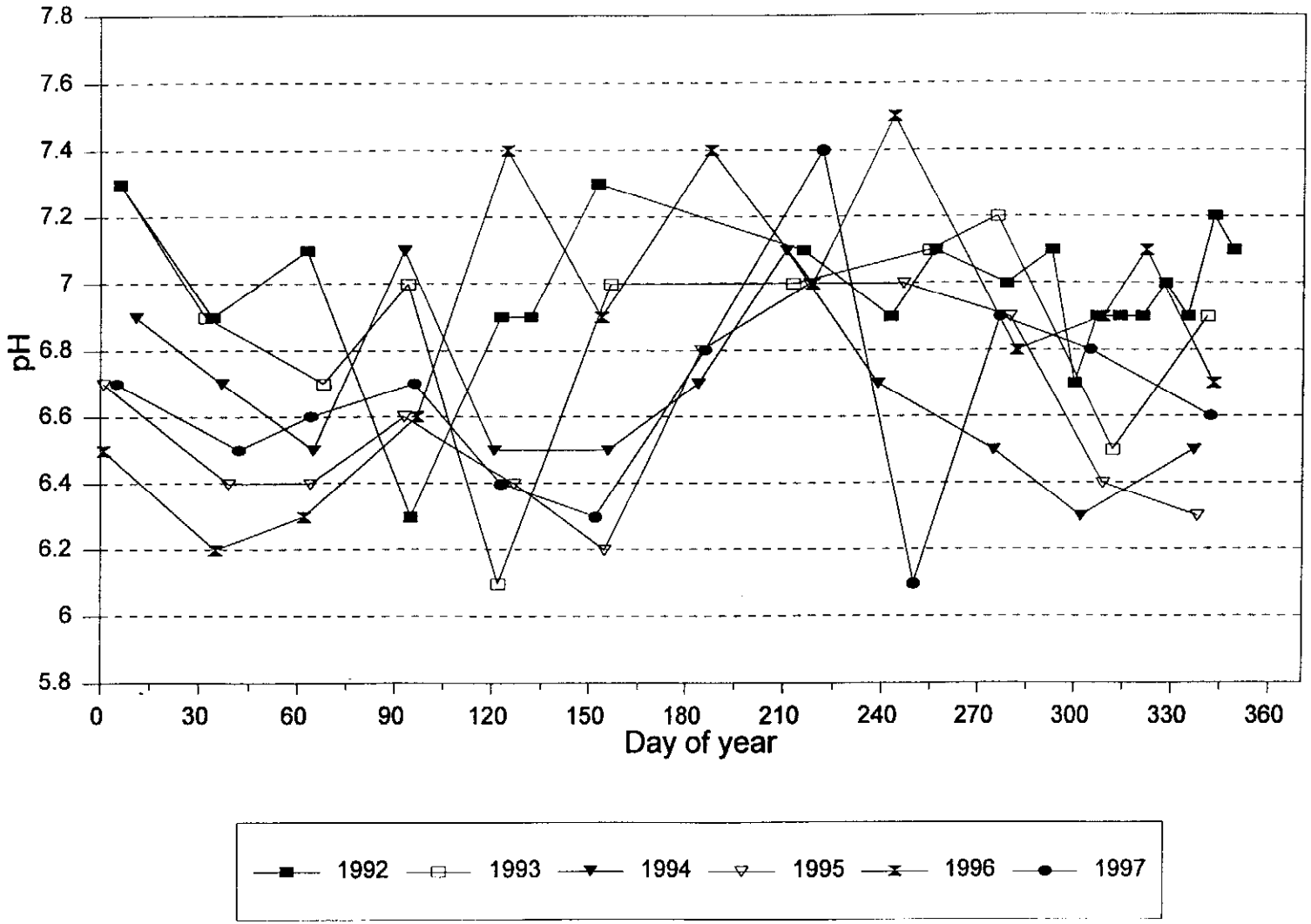


Fig. 2a: River below Hydro Plant

Zinc Concentration, 1992-1997

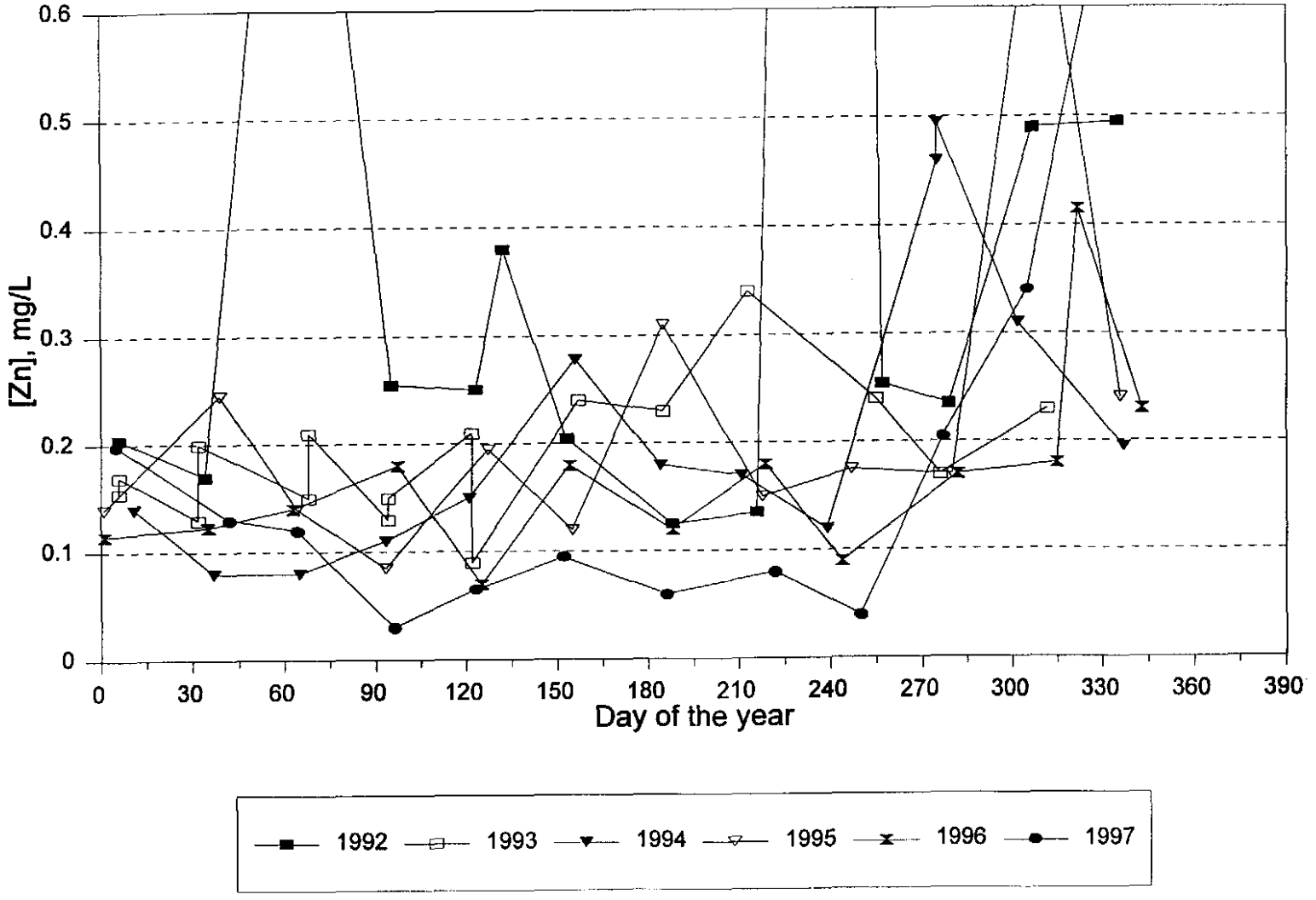


Fig. 2b: River below Hydro Plant

pH, 1992-1997

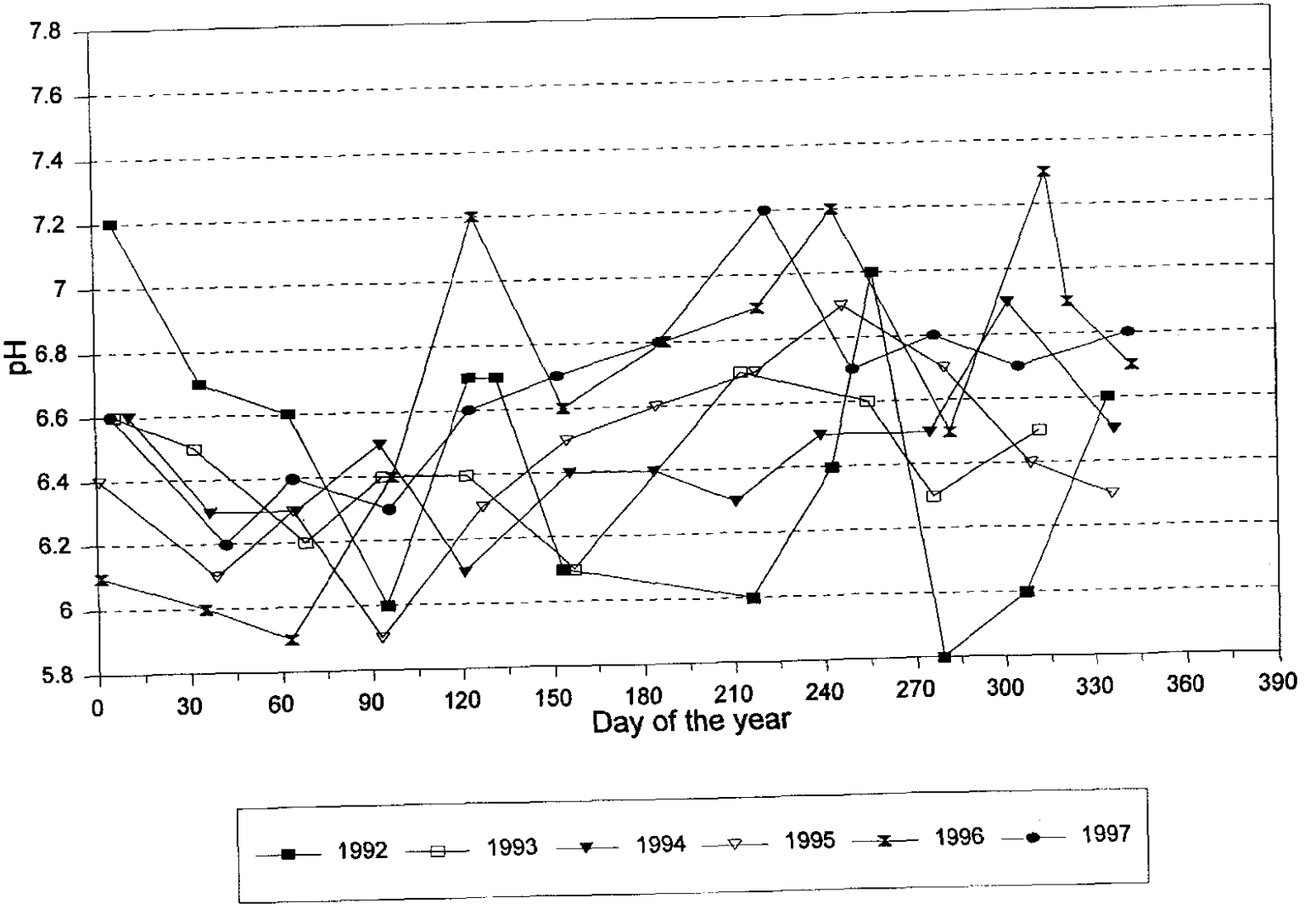


Fig. 3a: Simms Brook

Zinc Concentration, 1992-1997

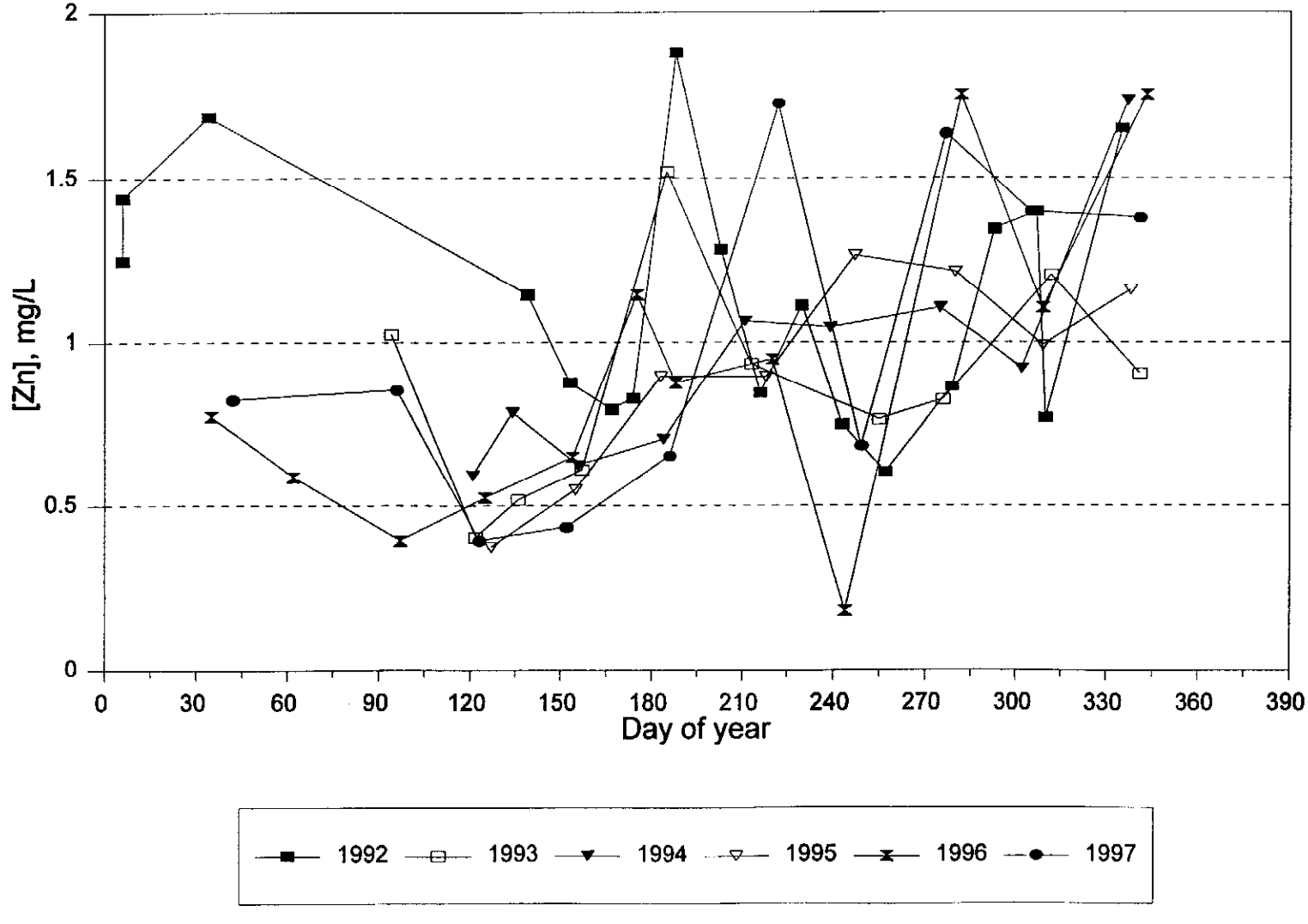


Fig. 3b: Simms Brook

pH, 1992-1997

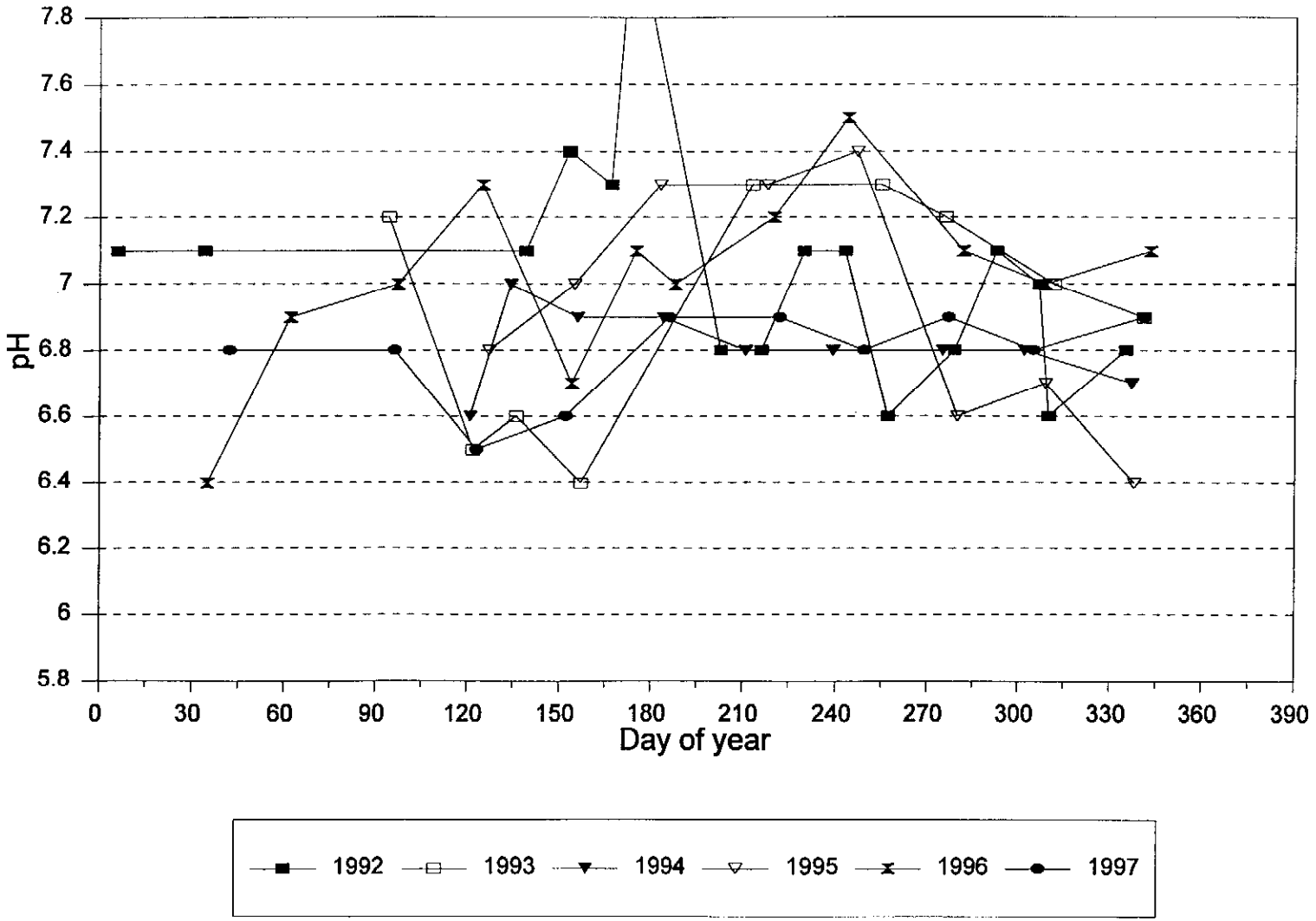


Fig. 4a: Tailing Pond 1

Zinc Concentration, 1992-1997

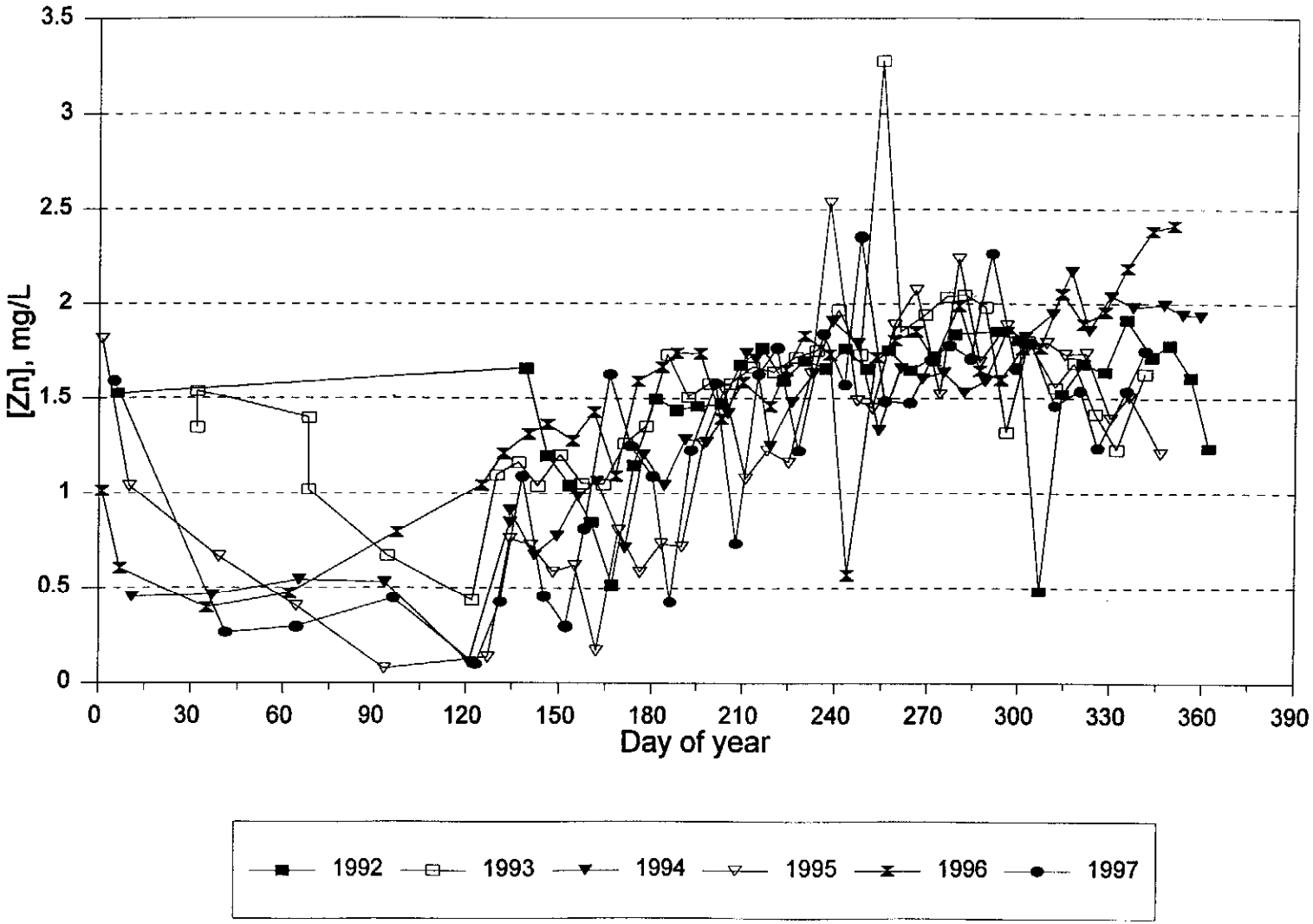


Fig. 4b:Tailing Pond 1

pH, 1992-1997

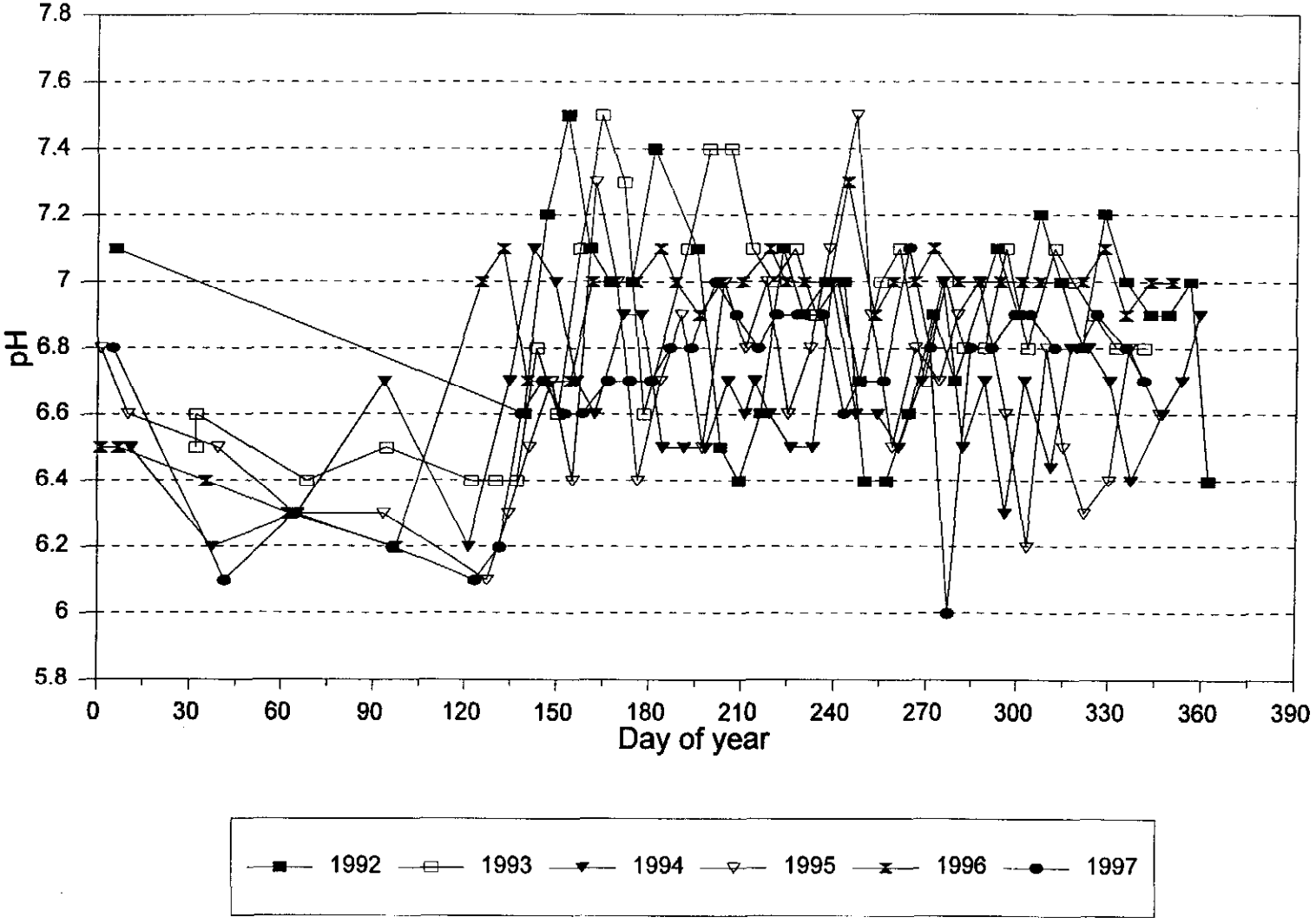


Fig. 5a: Tailing Pond 2

Zinc Concentration, 1992-1997

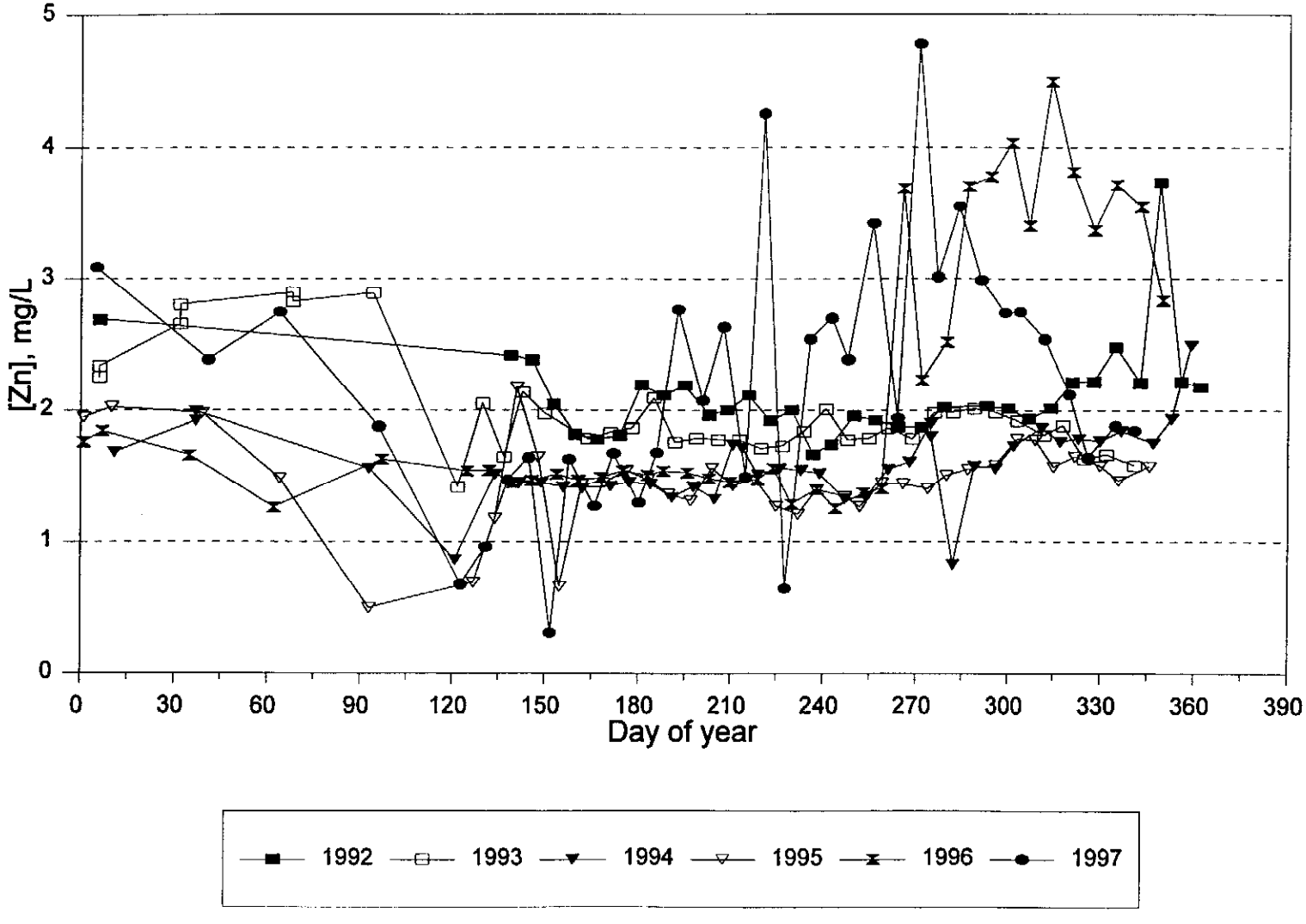


Fig. 5b: Tailing Pond 2

pH, 1992-1997

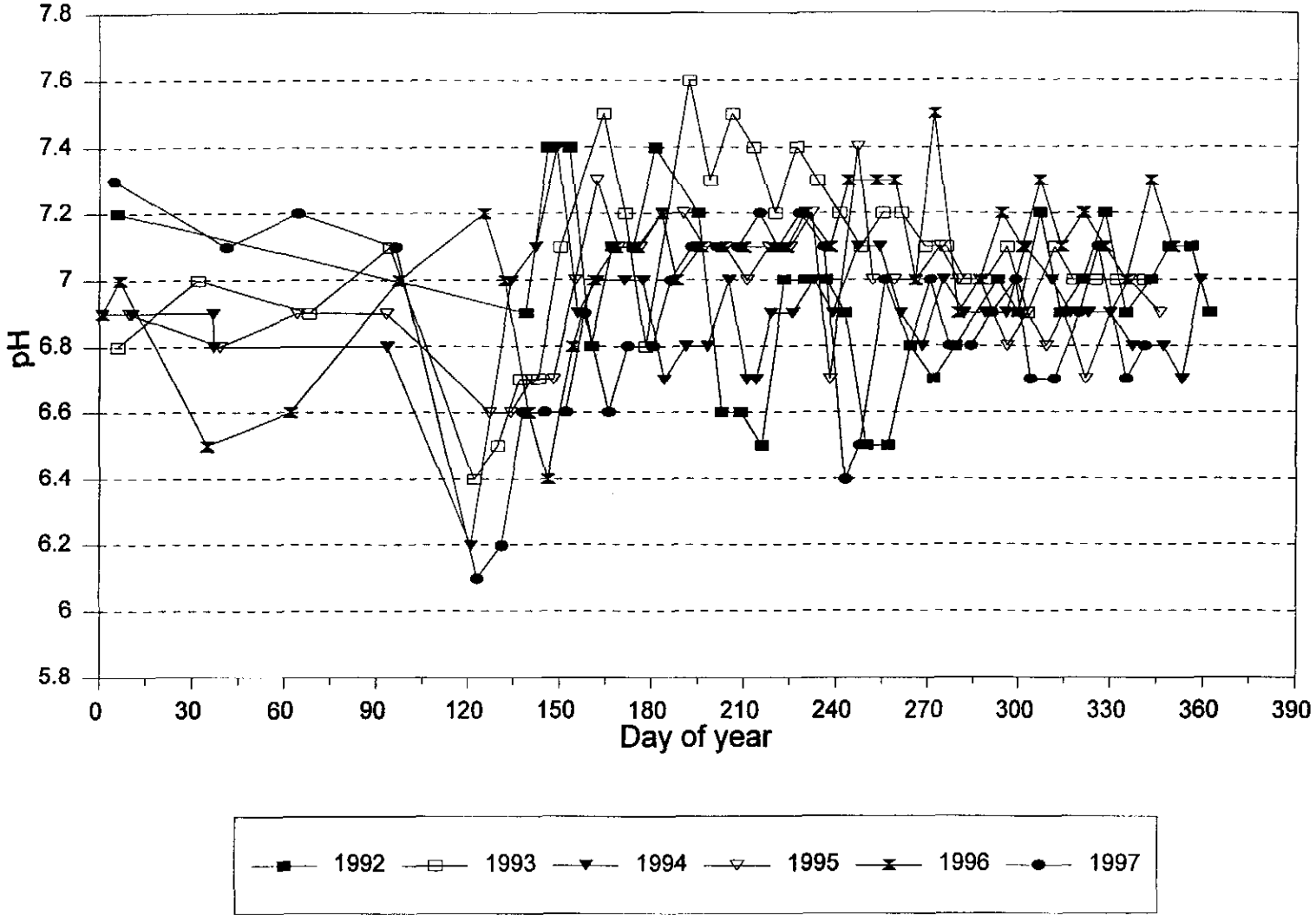


Fig. 6a: Drainage Tunnel

Zinc Concentration, 1992-1997

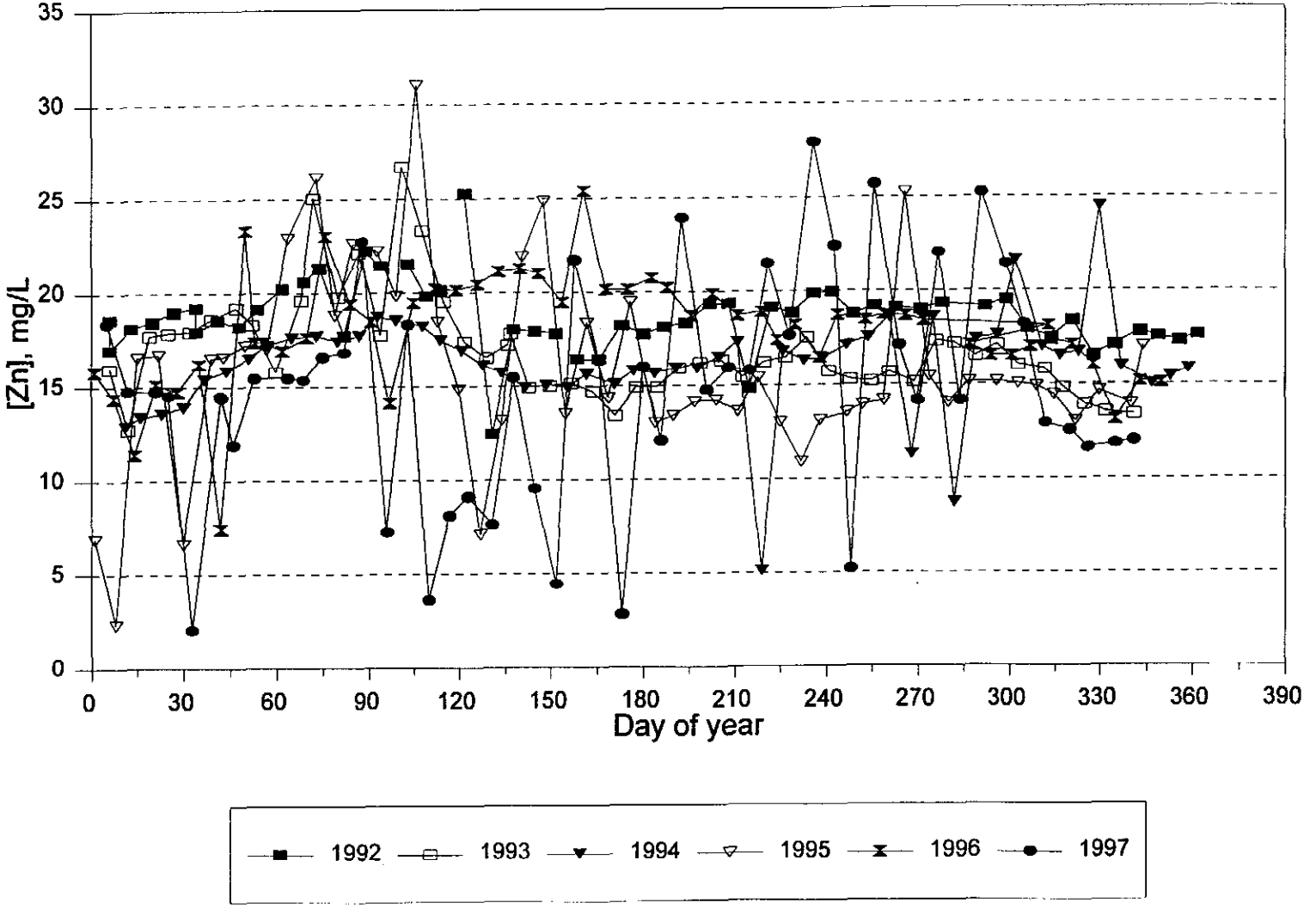


Fig. 6b: Drainage Tunnel

pH, 1992-1997

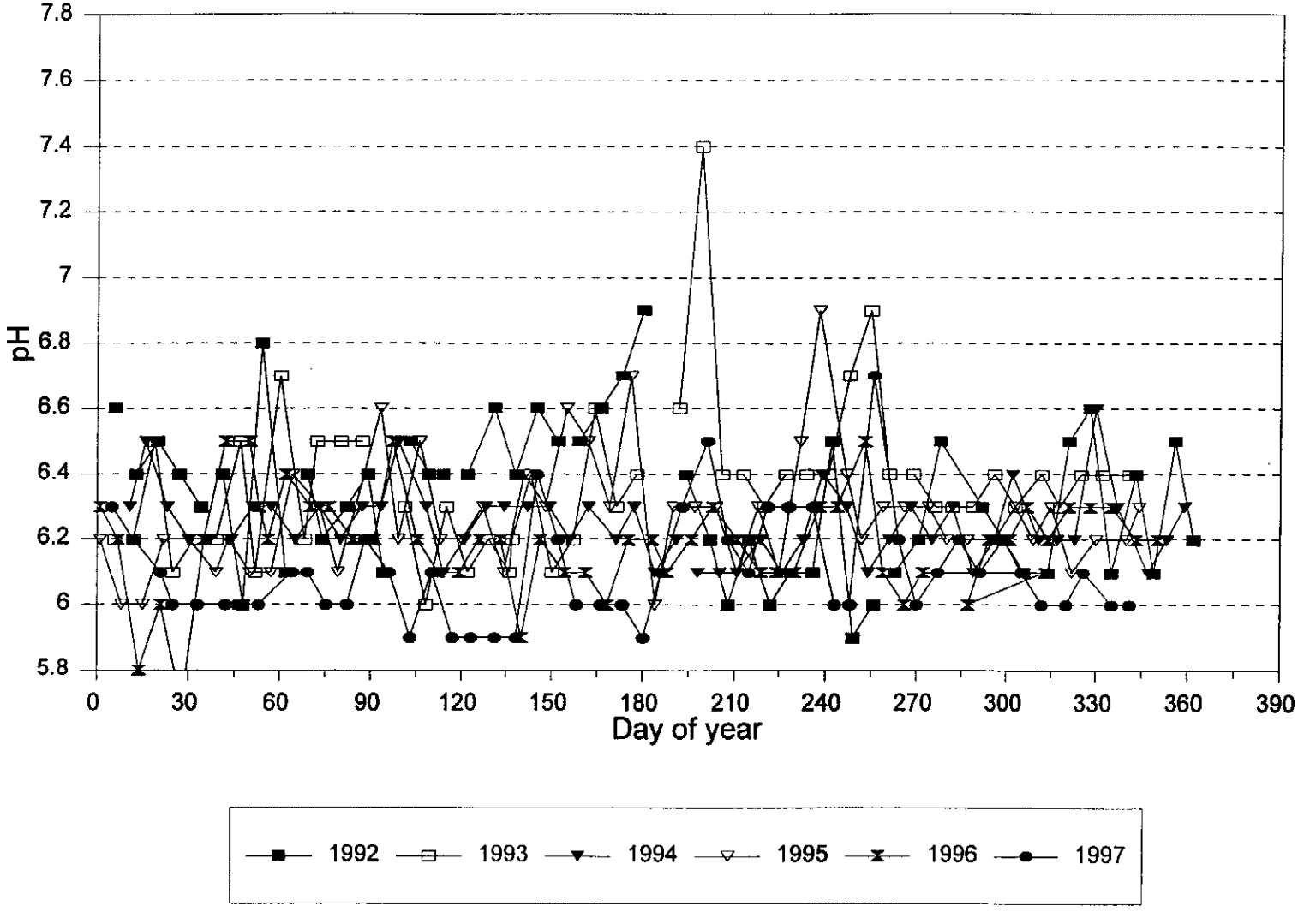


Fig. 6c: Drainage Tunnel

Average [Zn], 1990 - 1997

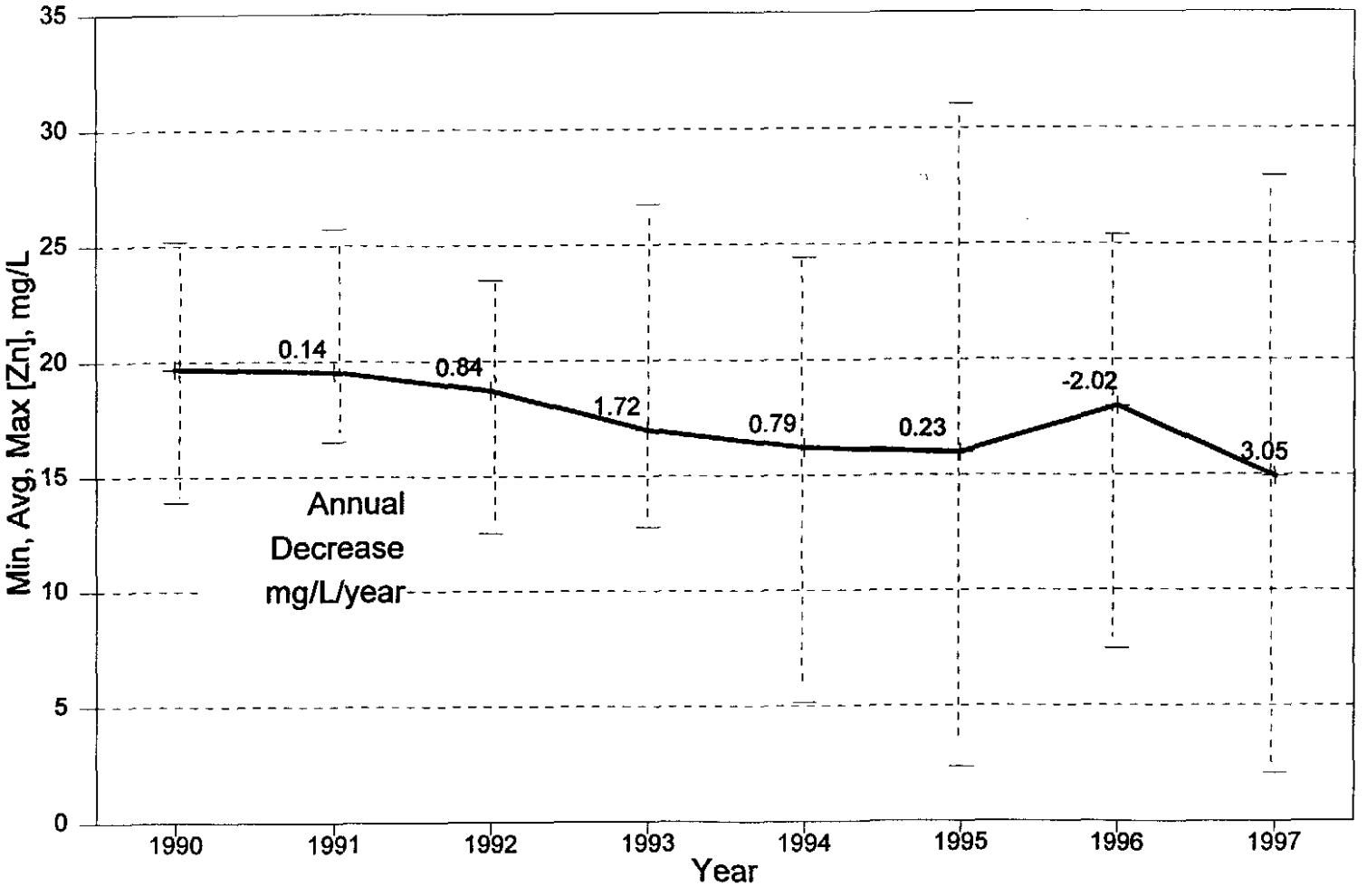


Fig. 6d: Drainage Tunnel

Flow, 1992-1997

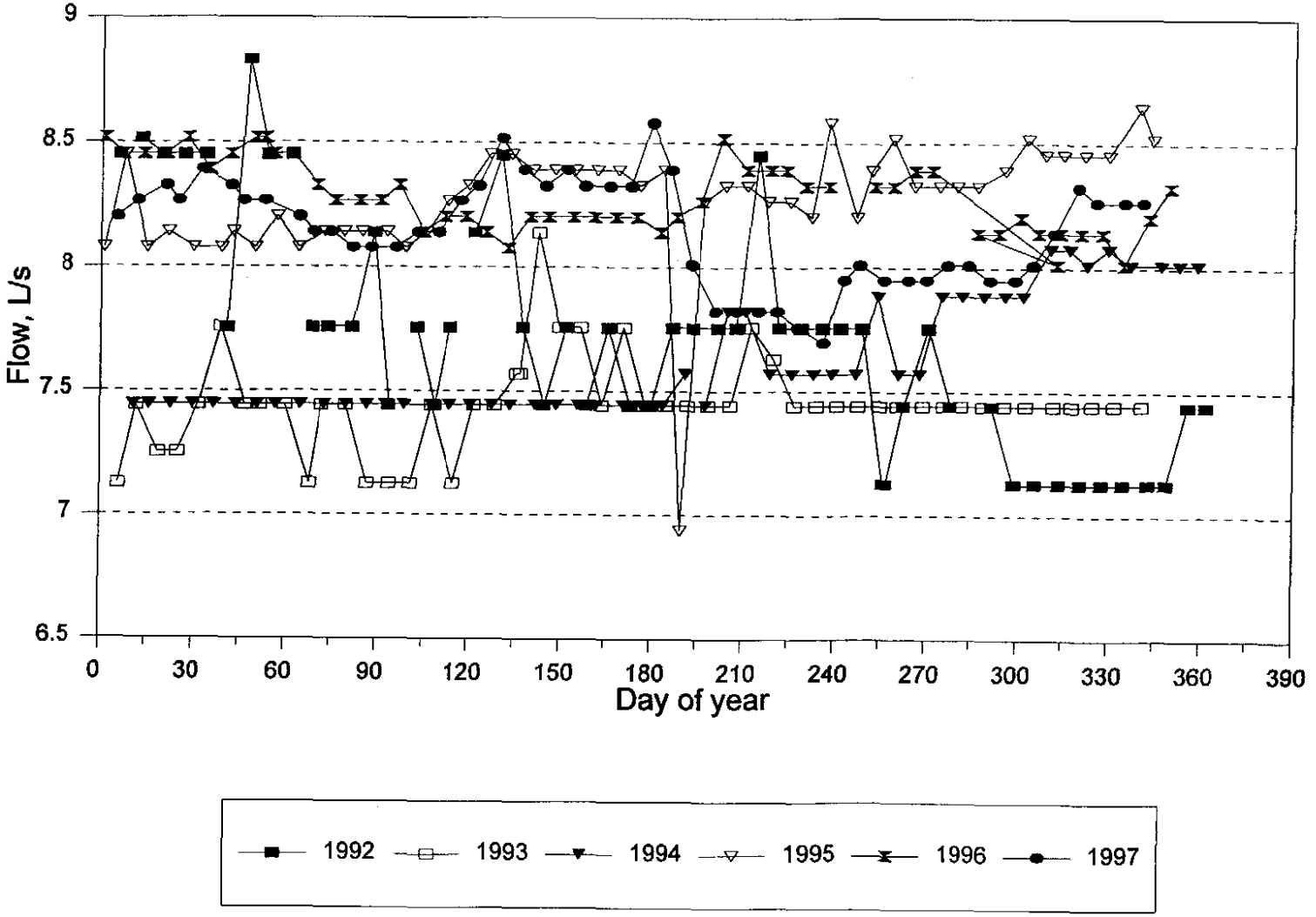


Fig. 6e: Drainage Tunnel

Average Flow, 1990 - 1997

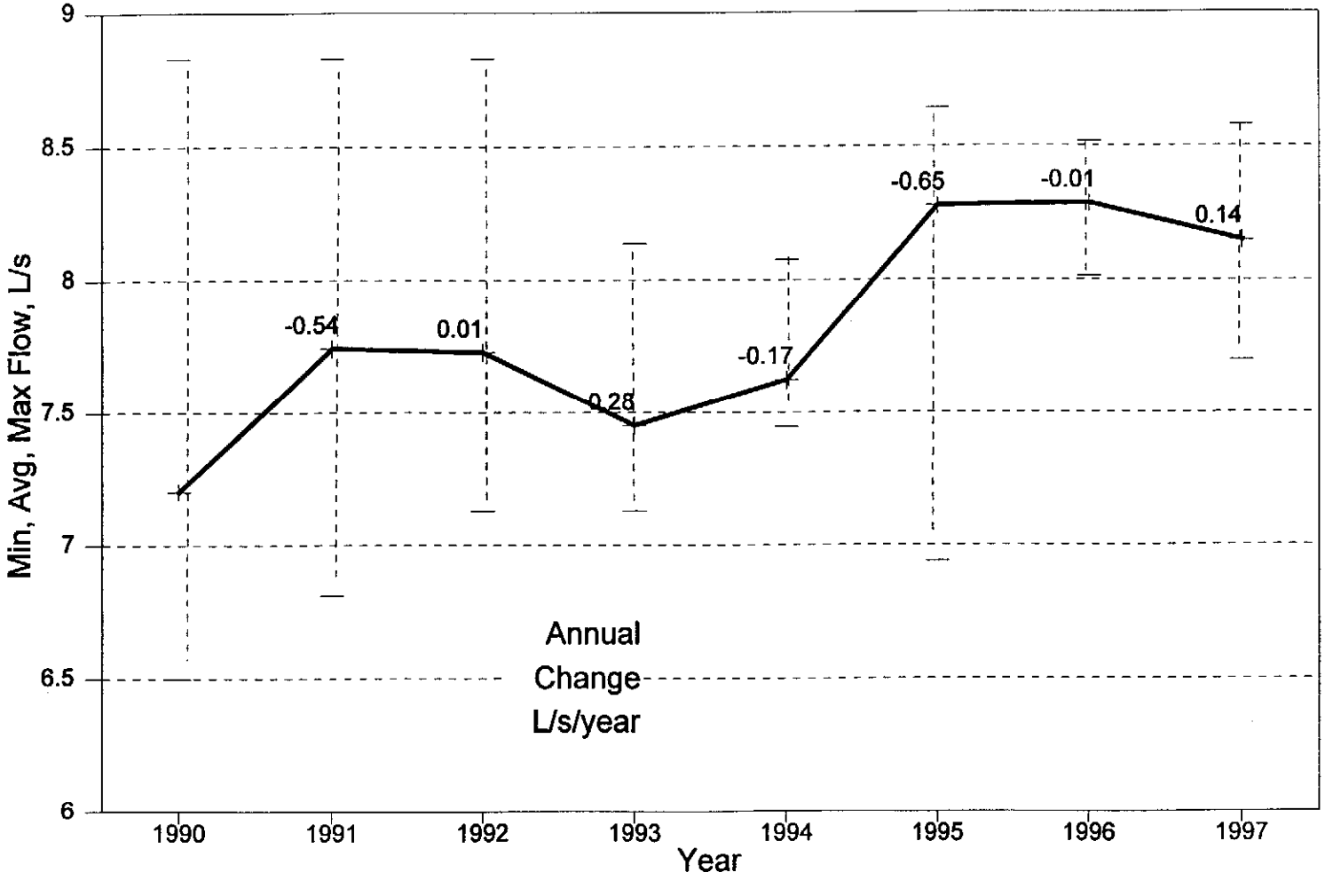


Fig. 7a: Oriental West Pit

Zinc Concentration, 1992-1997

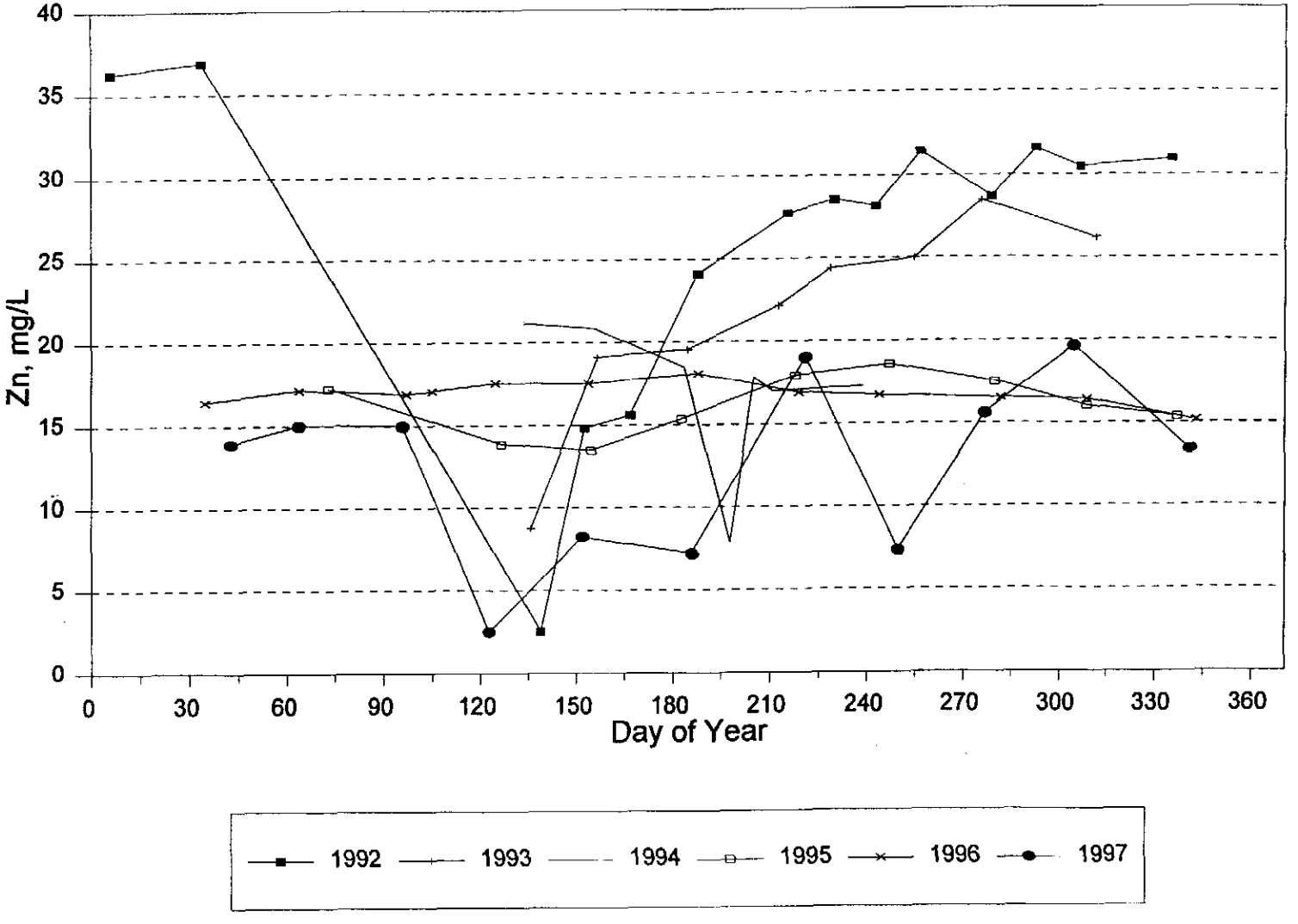


Fig. 7b: Oriental West Pit

pH, 1992-1997

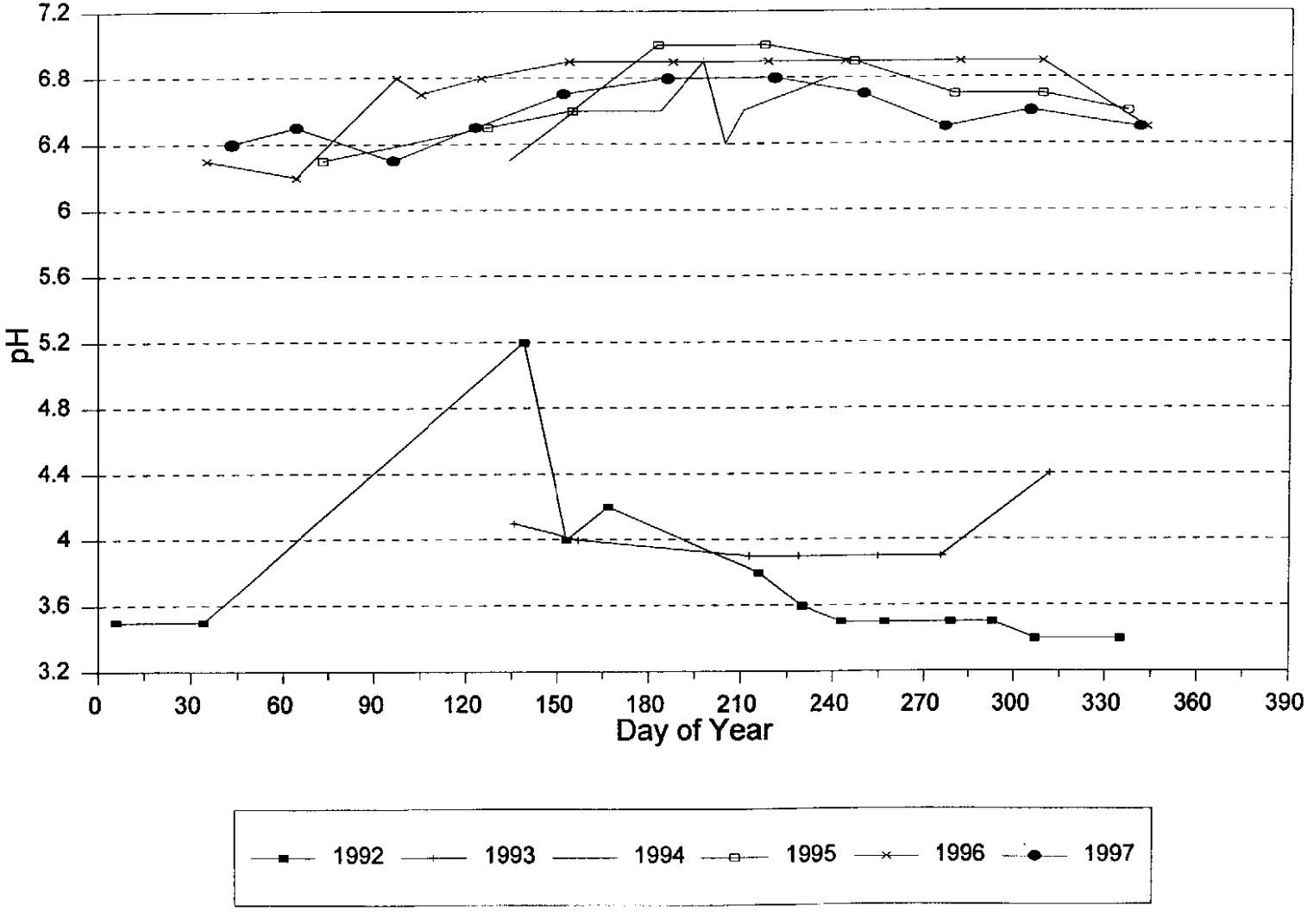


Fig. 8a: Oriental East Pit

Average [Zn], 1989 - 1997

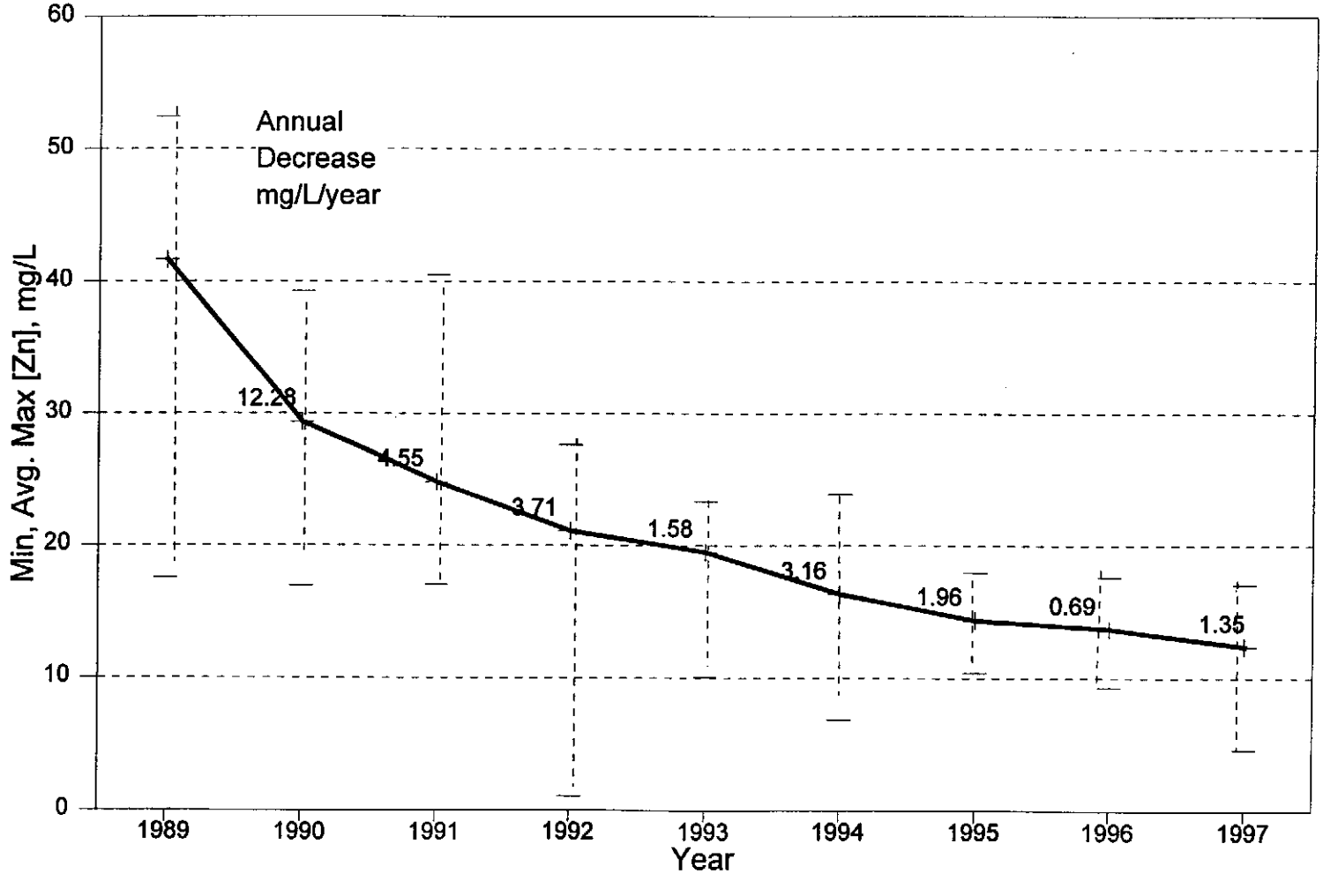


Fig. 8b: Oriental East Pit

Zinc Concentration, 1995-1997

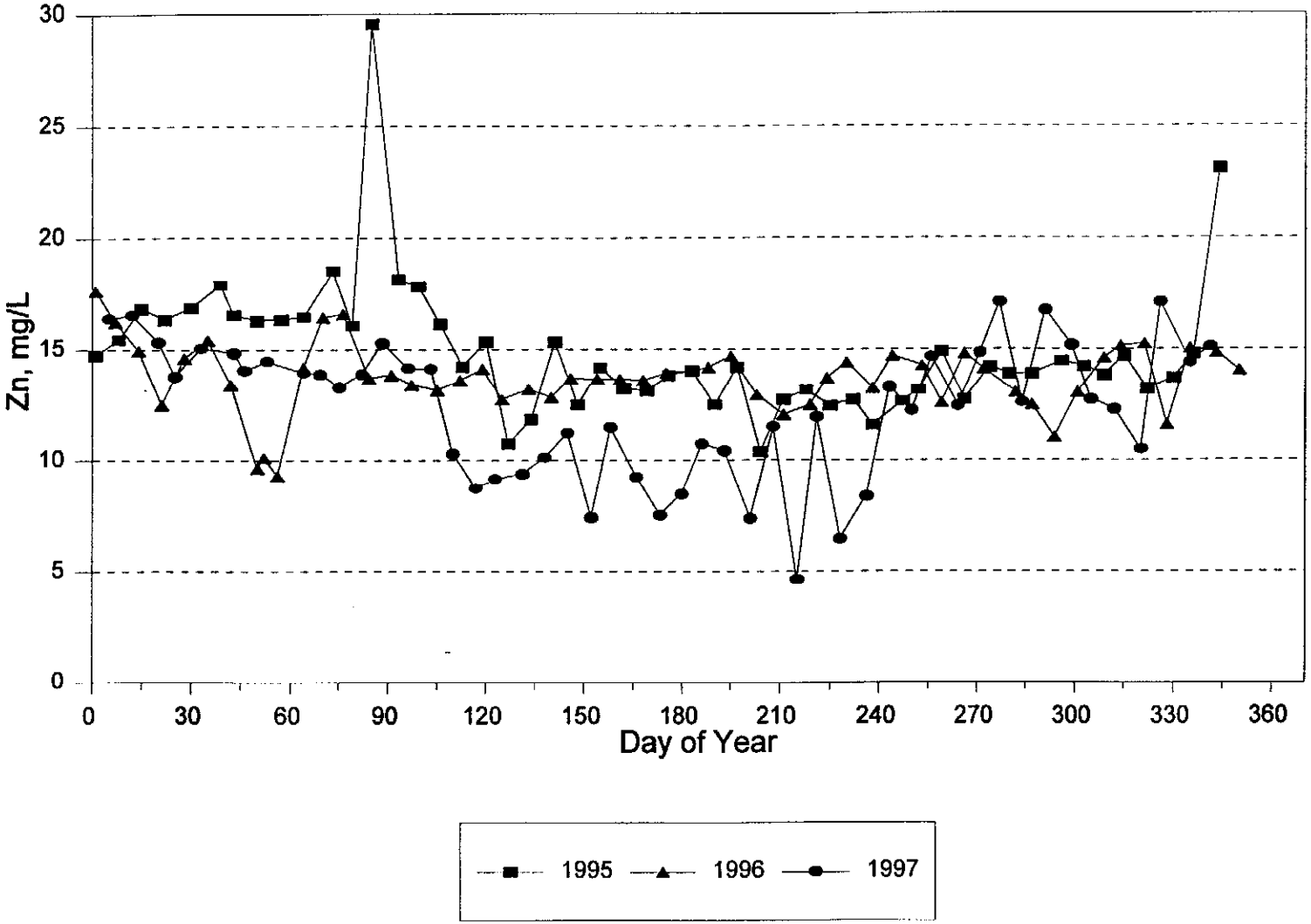


Fig. 8c: Oriental East Pit

Zinc Concentration, 1995-1997

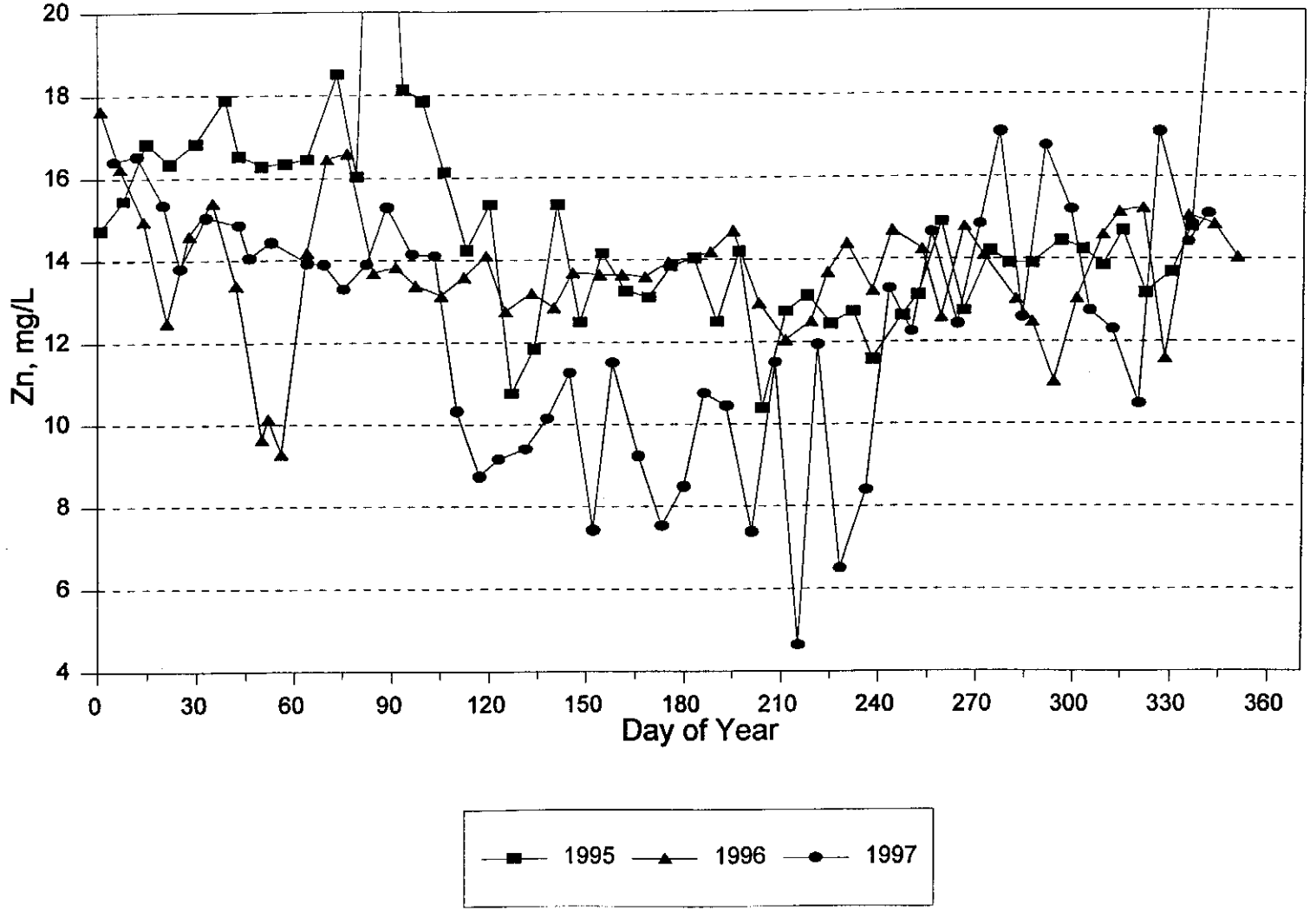


Fig.8d : Oriental East Pit

pH, 1996-1997

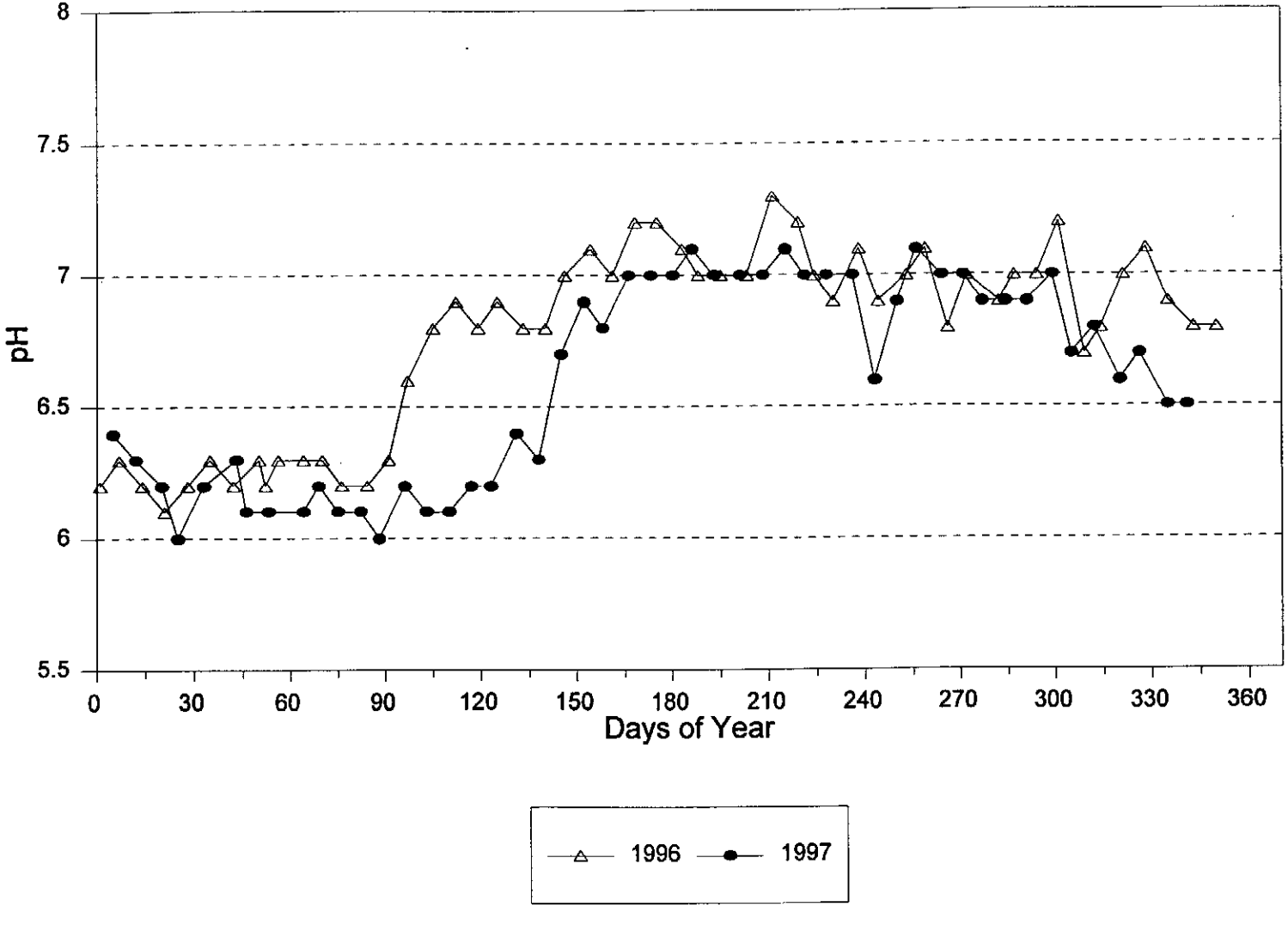


Fig. 9a: Lucky Strike Glory Hole

Average [Zn], 1991 - 1997

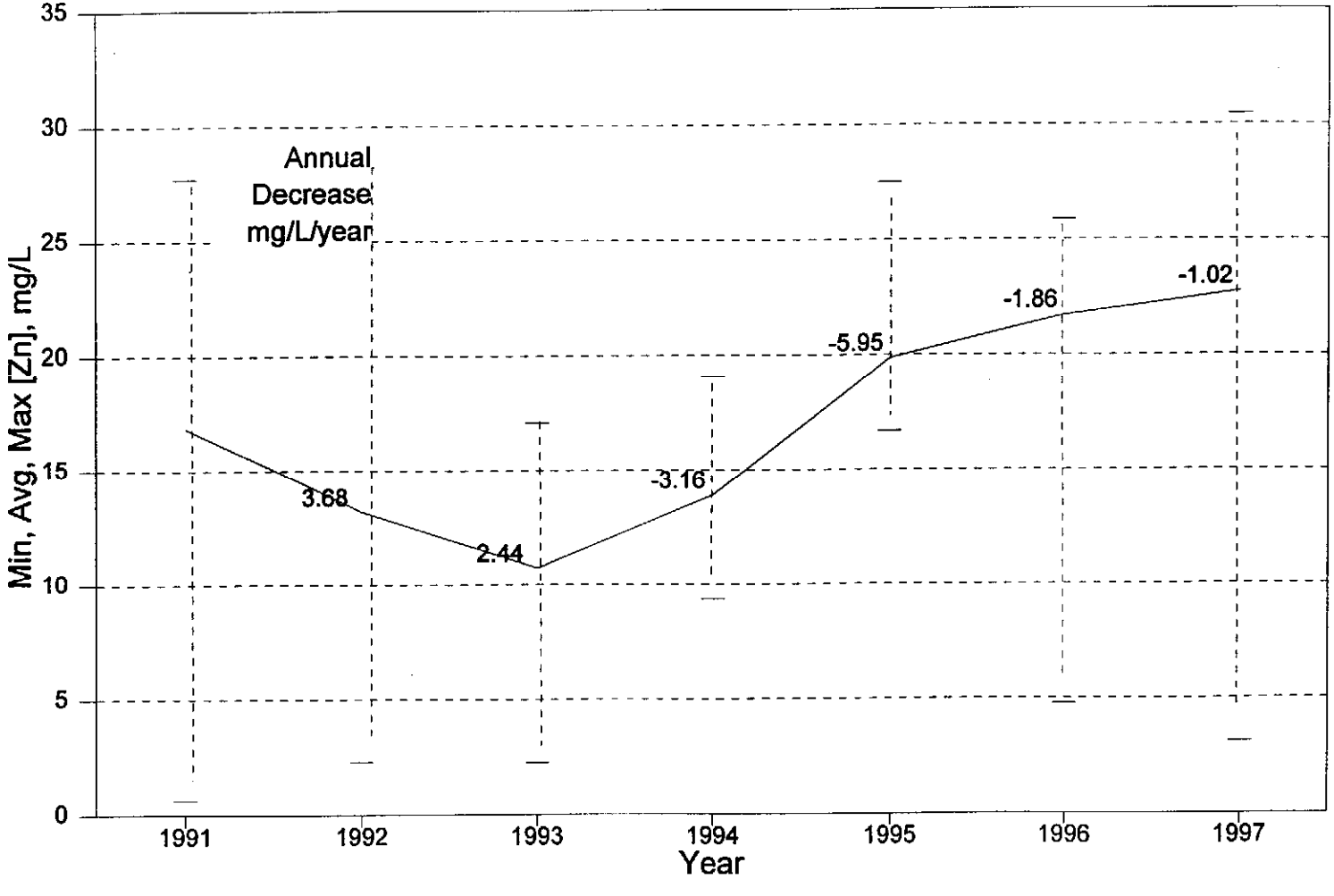


Fig. 9b: Lucky Strike Glory Hole

Zinc Concentration, 1992-1997

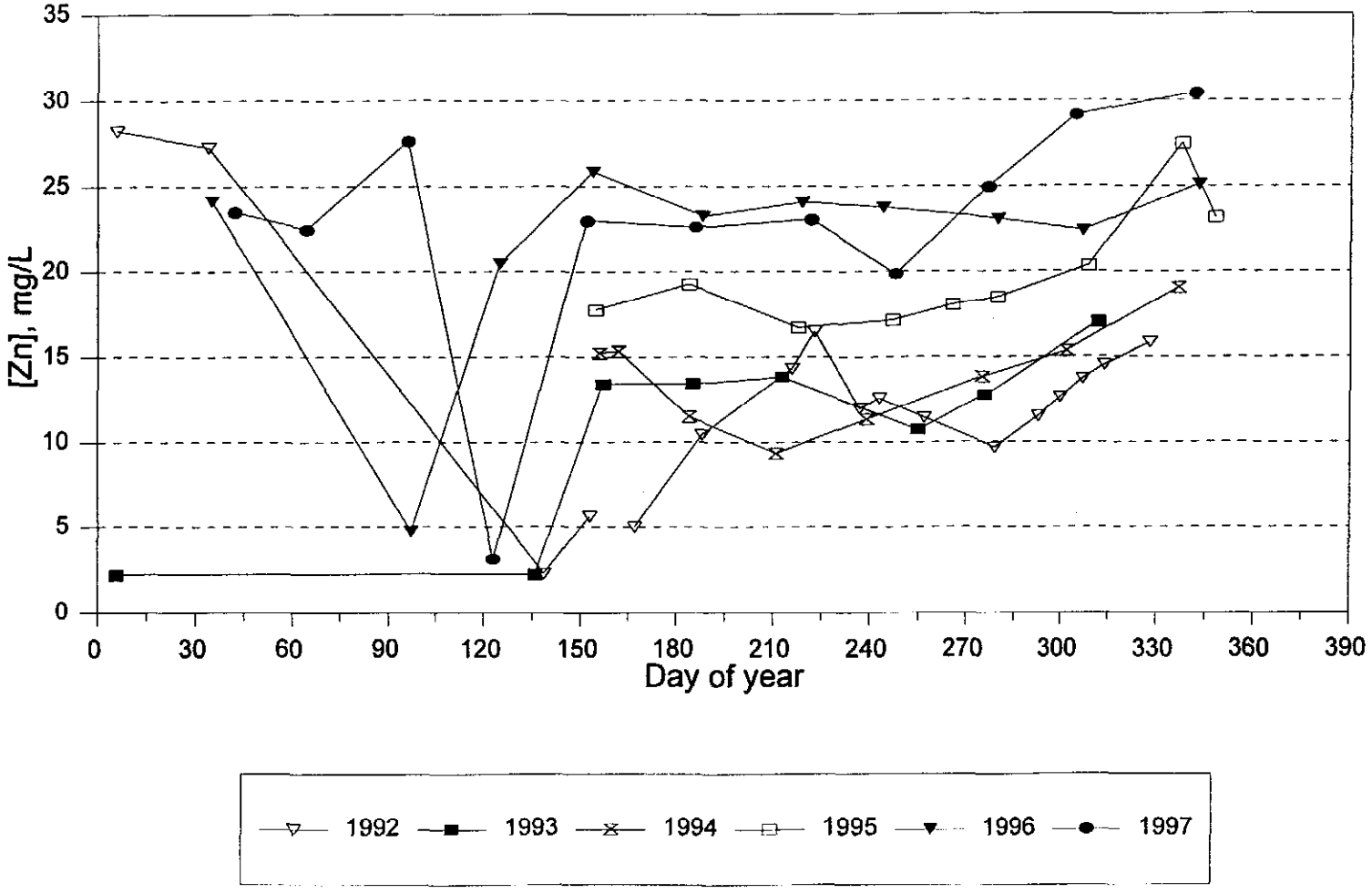
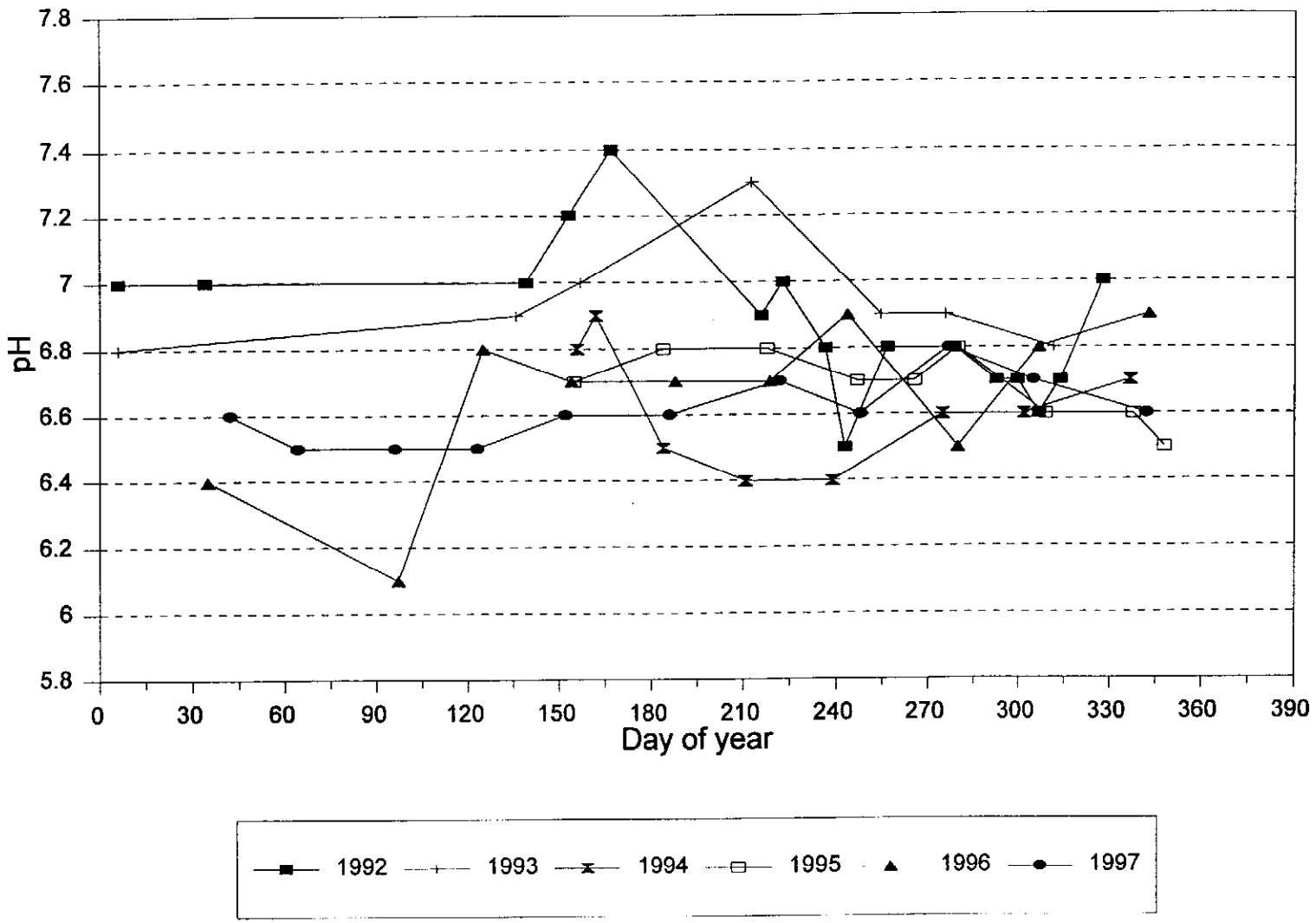


Fig. 9c: Lucky Strike Glory Hole

pH, 1992-1997



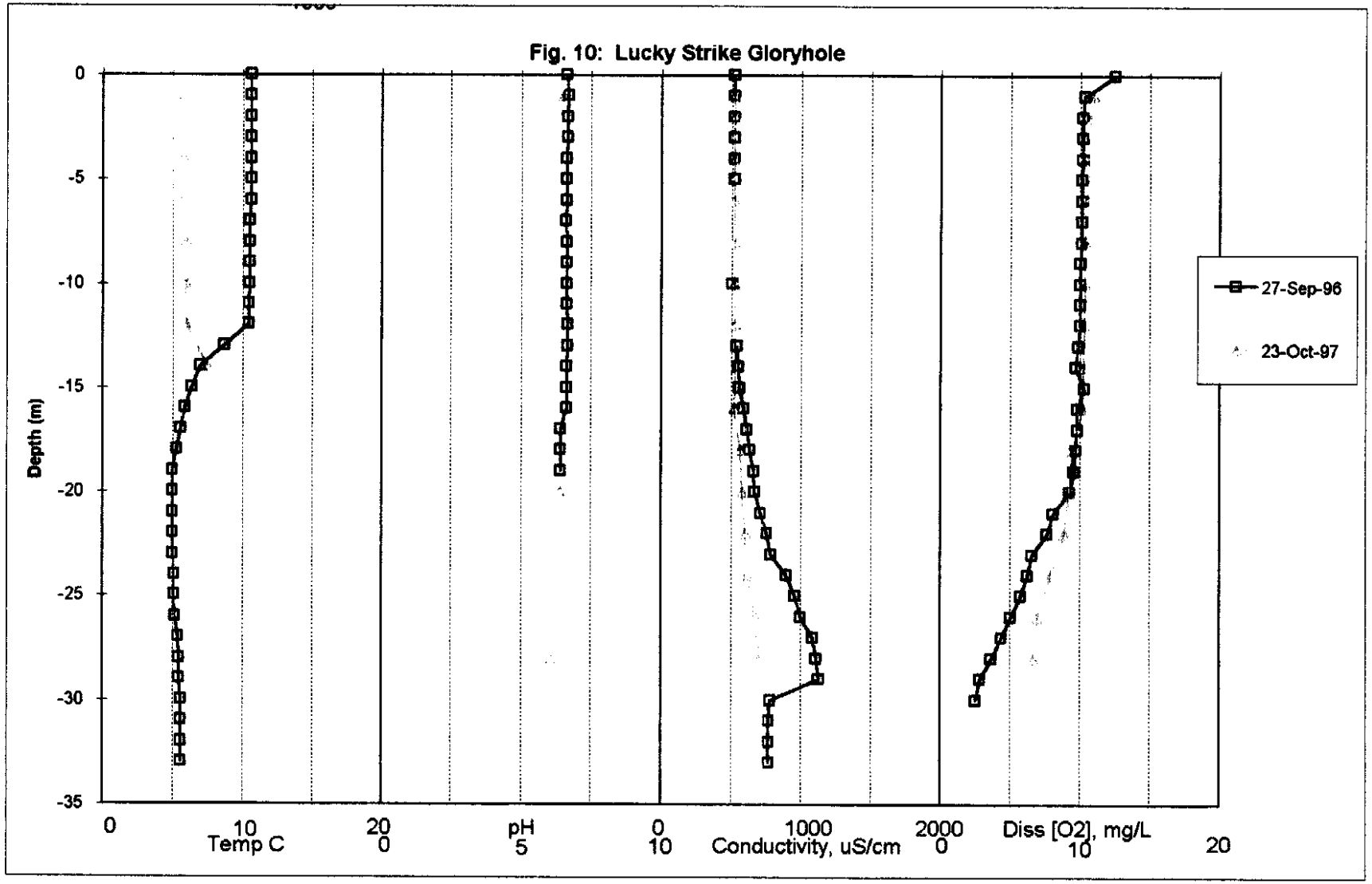


Fig. 10: Lucky Strike Gloryhole
Depth (m)
0
-5
-10
-15
-20
-25
-30
-35
0
10
20
Temp C
0
pH
5
10
0
1000
2000
Conductivity, uS/cm
0
Diss [O2], mg/L
10
20
27-Sep-96
23-Oct-97

Fig. 12: Oriental East Pit

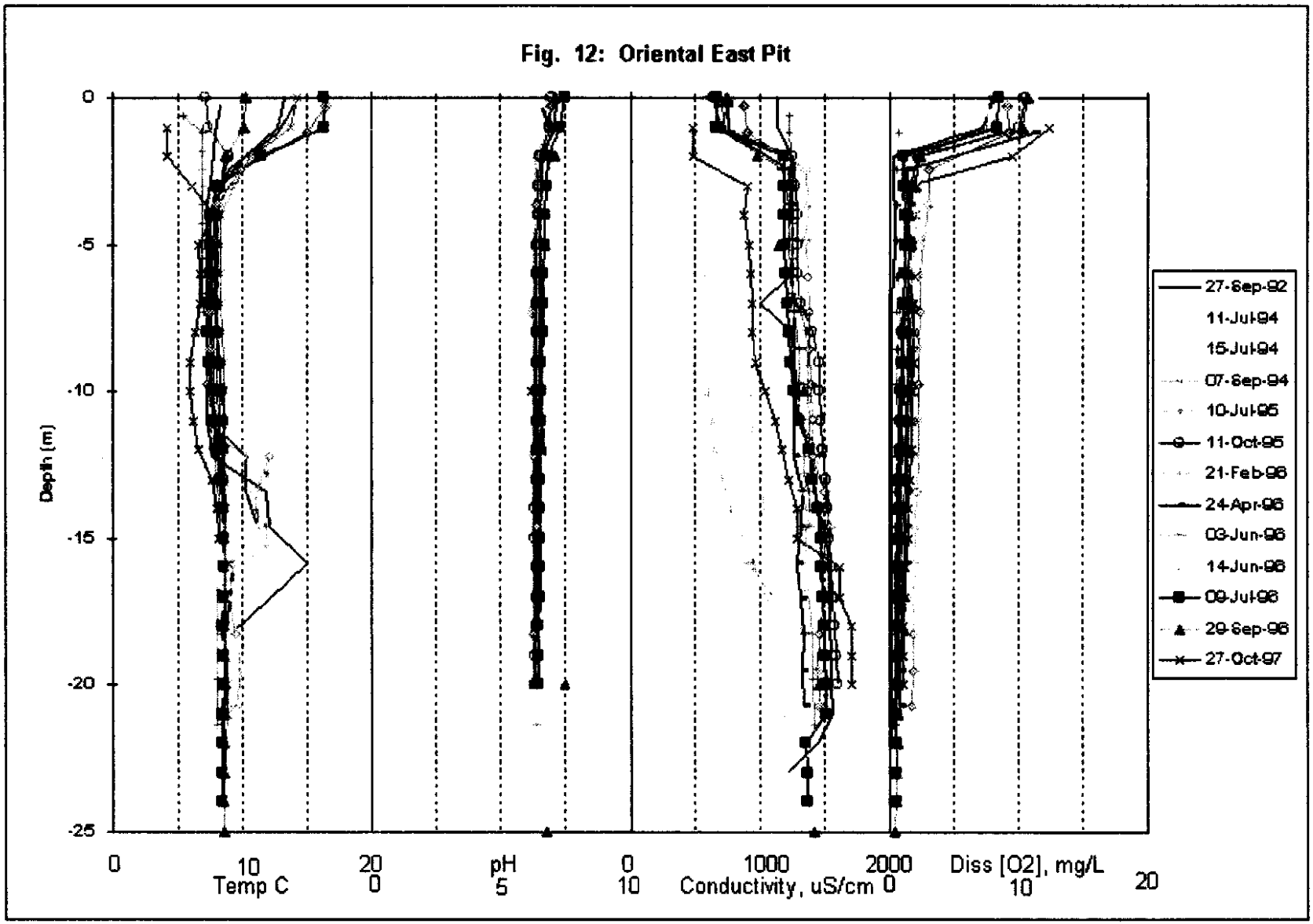


Fig. 13: Zinc Load, 1996-1997
OEP Weir and Final Effluent

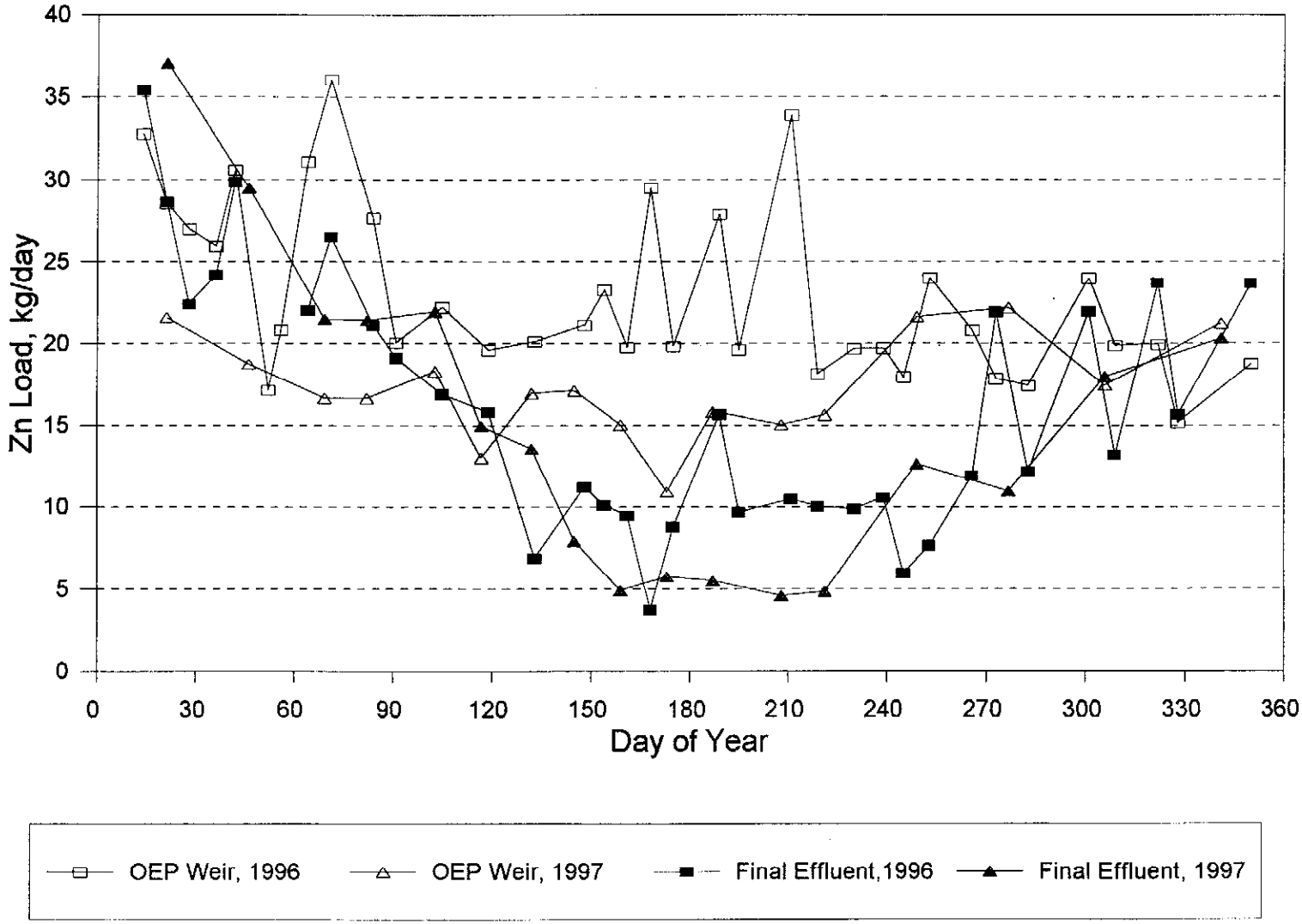


Fig. 14: Zinc Load, 1996-1997
PP10 and PP13

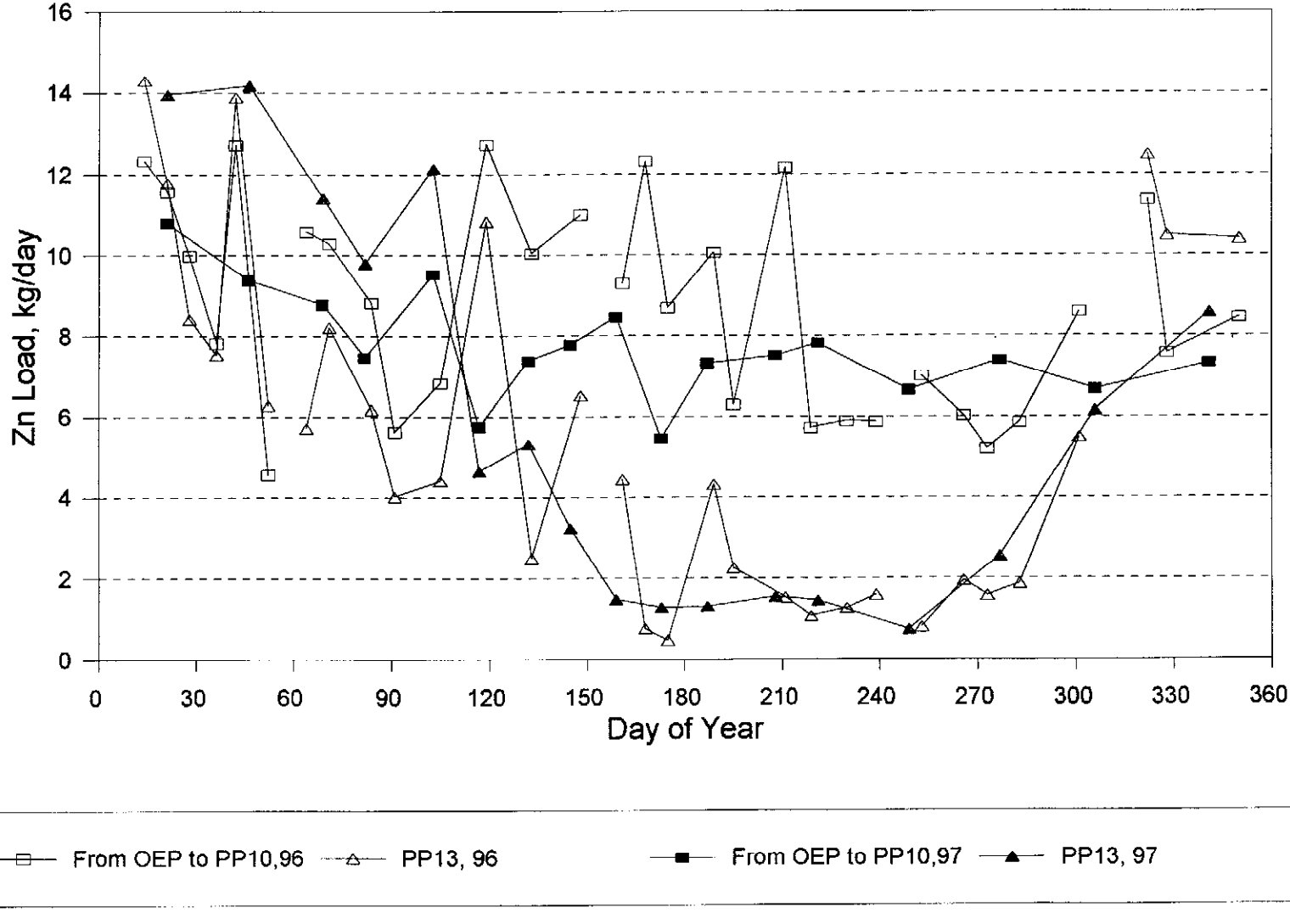


Fig. 15: Zinc Load, 1996-1997
PP14 and PP17

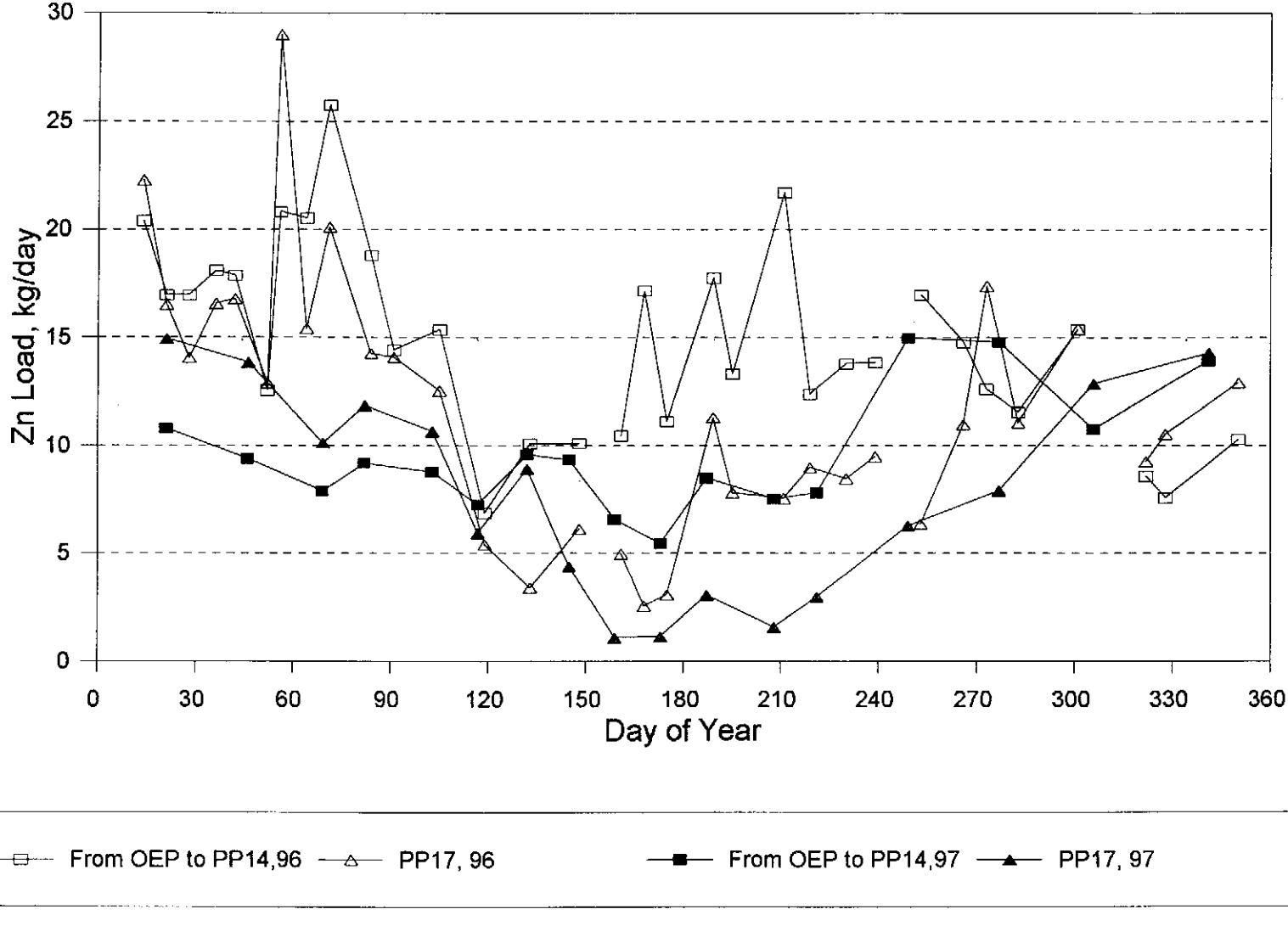


Fig. 16: Pond Performance
1995 - 1996-1997

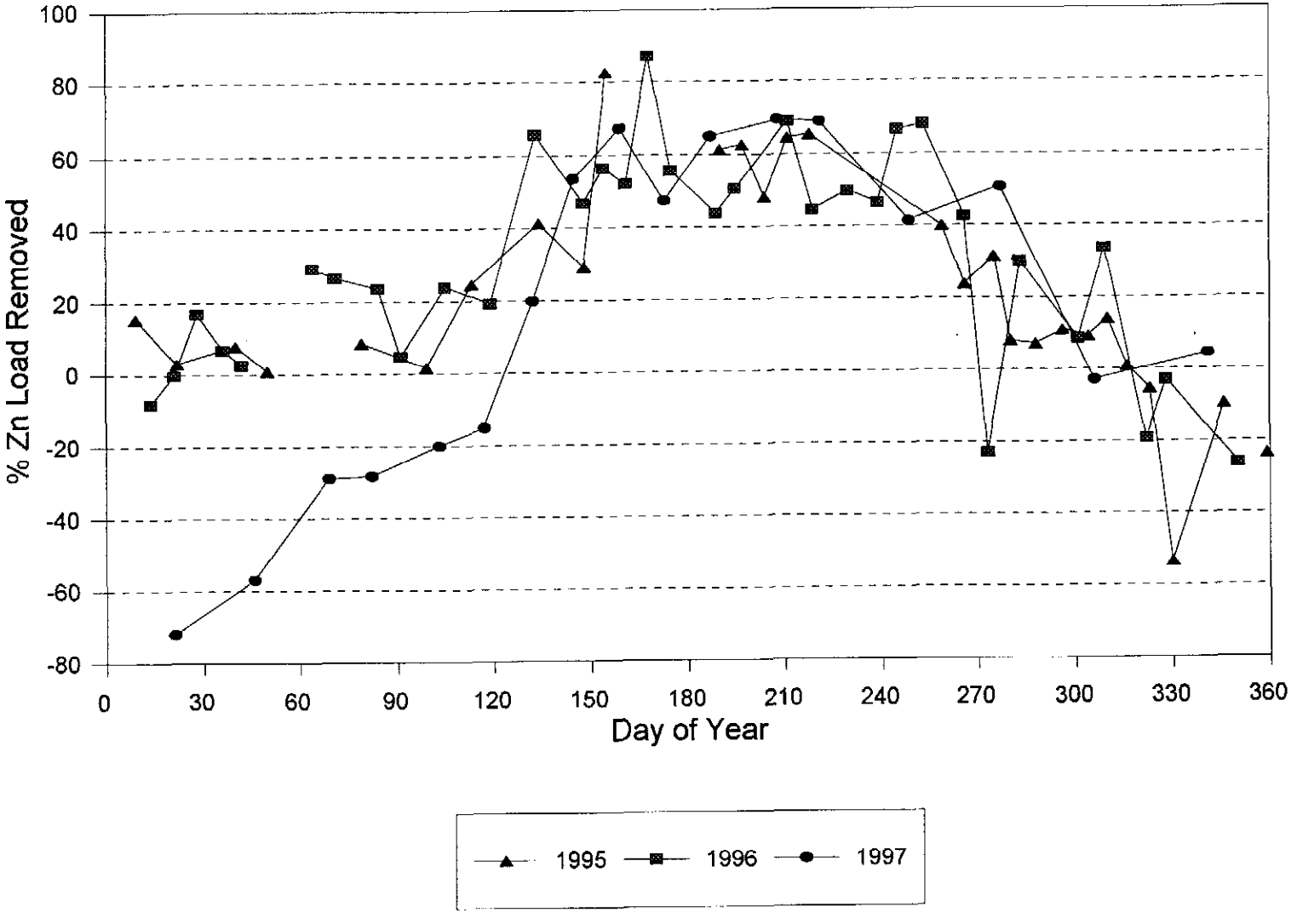


Fig. 17: pH, 1996-1997
OEP Weir, Final Effluent, PP13, PP17

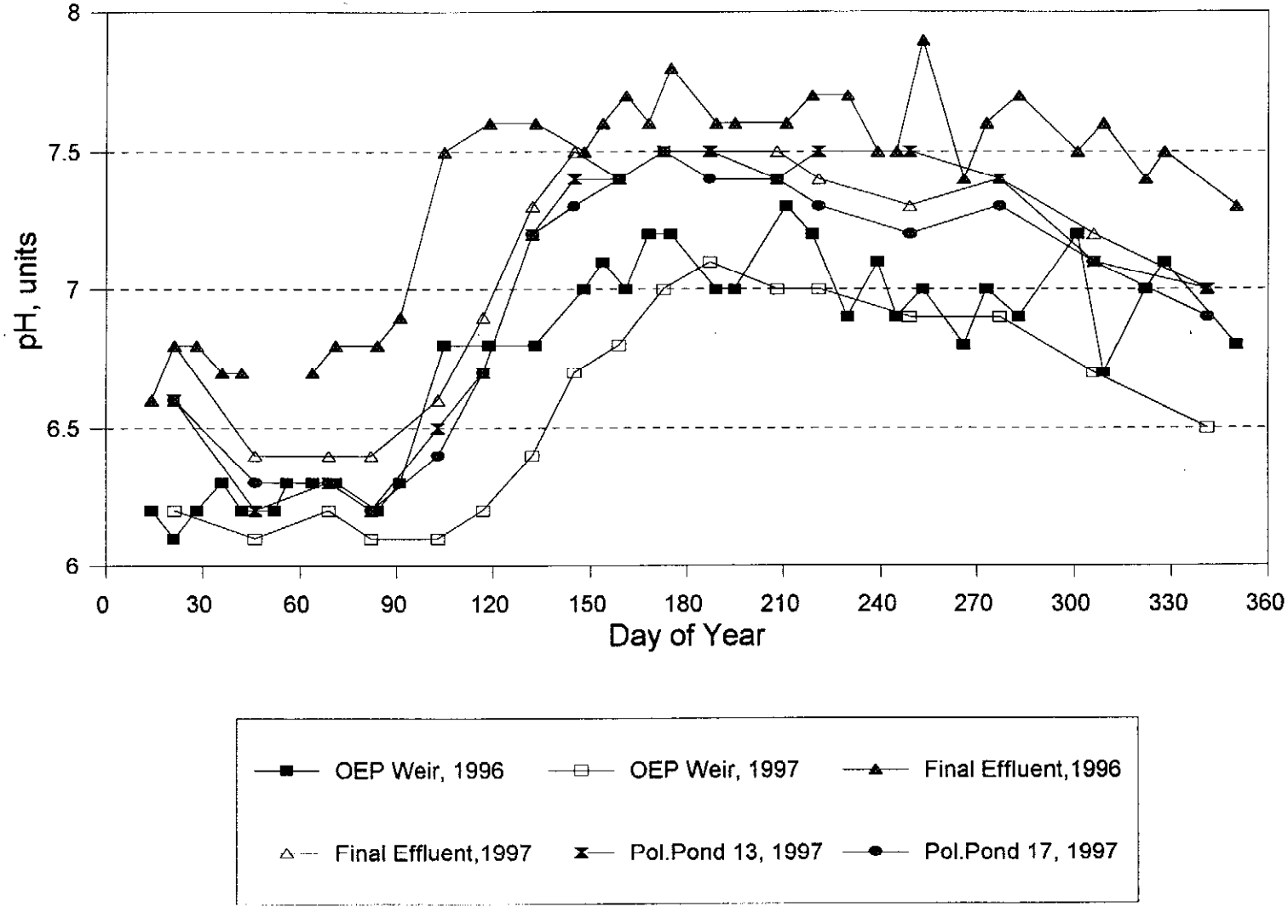


Fig. 18: Zinc Concentration, 1996-1997

OEP Weir and Final Effluent

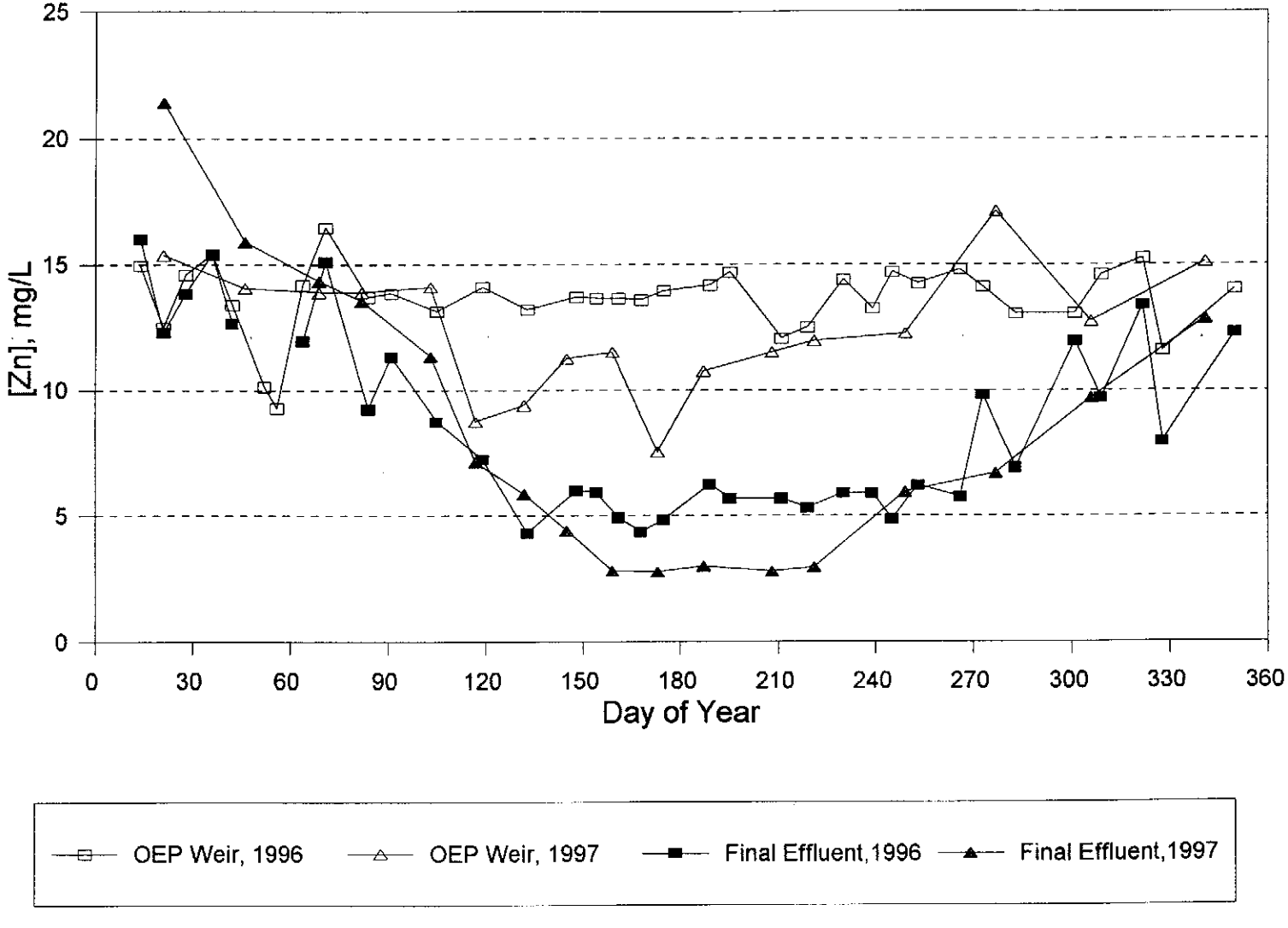


Fig. 19: Zinc Concentration, 1996-1997

OEP Weir,Final Effluent, PP13 and PP17

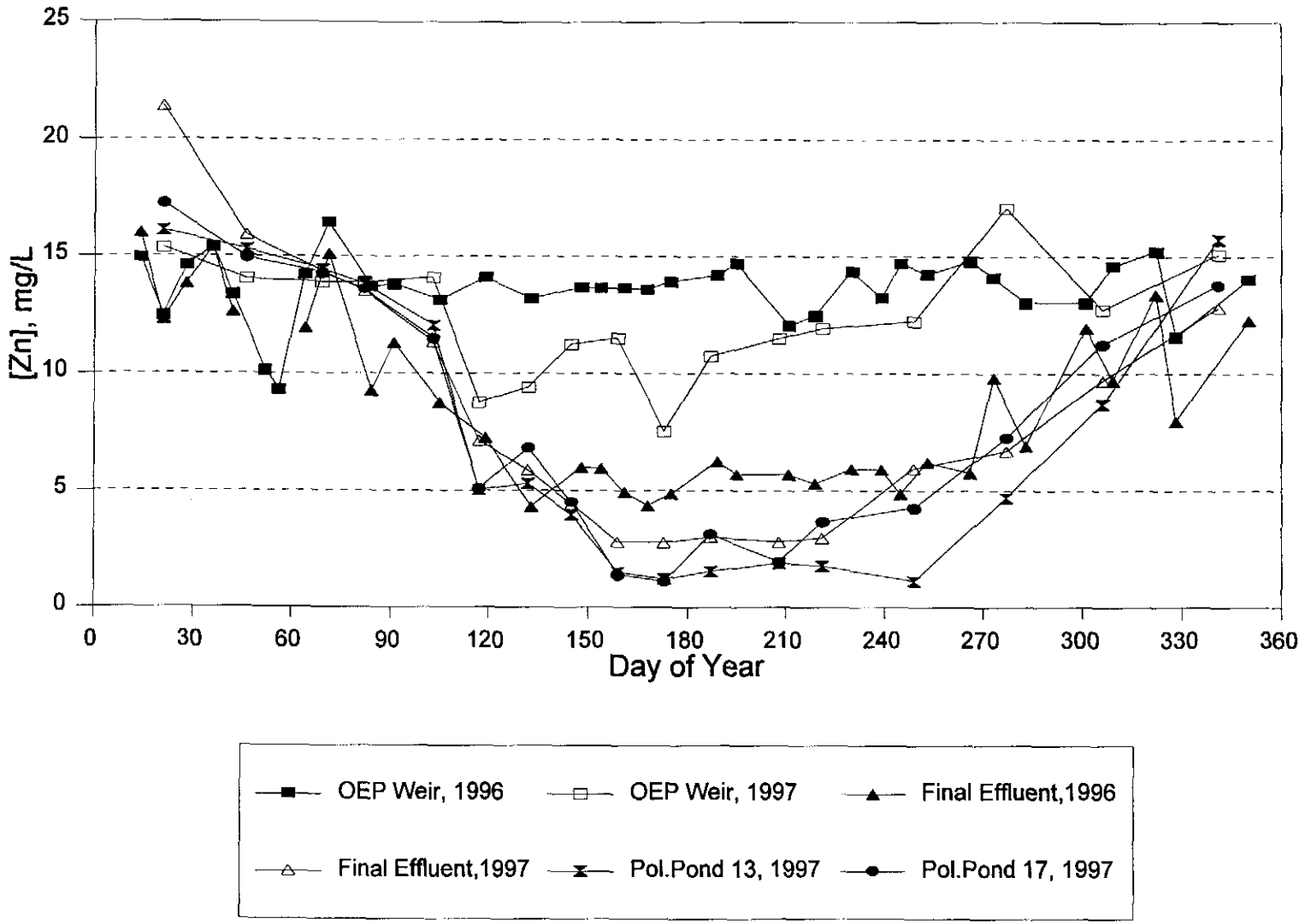
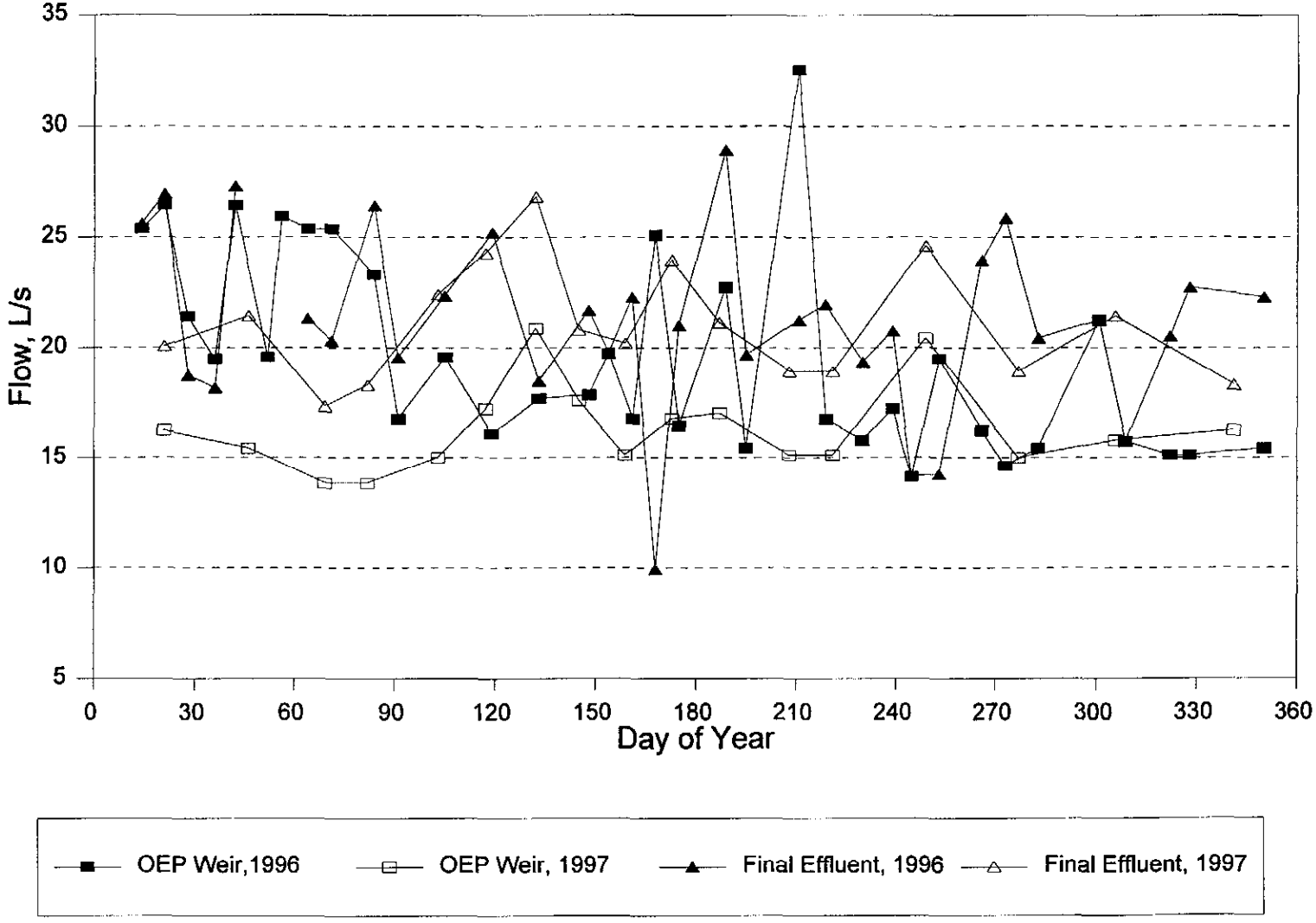


Fig. 20: FLOW, 1996-1997

OEP Weir and Final Effluent



Appendix 3

Table 1: Summary of Sedimentation Trap Data for OEP and OWP.

				Sedimentation Rate, $g.m^{-2}.d^{-1}$									
				OEP						OWP		Lucky Strike	
			Summer	Outflow		4 m	11 m	20 m		2m	7 m	5 m	17 m
From	To	Days	Period?	A	B			A	B				
20-Sep-90	22-Oct-90	32	Yes	0.62				2.1					
20-Sep-90	28-May-91	250			2.1				5.4				
22-Oct-90	28-May-91	218		4.6				4.6					
28-May-91	18-Oct-91	143	Yes	1.9				5.3					
18-Oct-91	29-Sep-92	347		3.8				19					
14-Jun-93	30-Aug-93	77	Yes			5.9	9.9						
30-Aug-93	11-Jul-94	315				5.1	4.5						
11-Jul-94	07-Sep-94	58	Yes								6.2		
07-Sep-94	07-Jul-95	303				3.9	3.2	12			4.9		
07-Jul-95	12-Oct-95	97	Yes			5.3	4.9	6.0			6.2		
12-Oct-95	10-Jul-96	272				4.5	4.5	60			43		
10-Jul-96	29-Sep-96	81	Yes			4.8	5.5	9.3			7.0		
29-Sep-96	23-Jul-97	297				ns	4.6	13			21		
23-Jul-97	09-Oct-97	78	Yes			ns	3.0						
23-Jul-97	22-Oct-97	91	Yes					2.3			4.1		
28-Aug-97	09-Oct-97	42	Yes									<dl *	<dl *
28-Aug-97	22-Oct-97	55	Yes							1.9			

< dl * non-detect reported according to October 9, 1997 sampling criteria.

Table 2: Sedimentation Rate Data and Calculations for OEP and OWP, 1990 to 1996.

Sedimentation Traps Placed	Retrieved	No. of Days in Period	Oriental East Pit (OEP) Sed. rate, kg.d^{-1}.pit^{-1} 20 m	4 m	11 m	Average Sedimentation kg.d^{-1}.pit^{-1}	kg.m^{-2}.d^{-1}	Sediment in period kg in period	Cumulative to date kg	Proportions for years *** (current,	prev/next)	Year	Estimate for year (to date) kg.y^{-1}	Oriental West Pit (OWP) 10 m S.T. kg.d^{-1}.pit^{-1}	kg.m^{-2}.d^{-1}	Sediment in period kg	Cumulative to date kg	Estimated for year kg.y^{-1}
20-Sep-90	22-Oct-90	32	40			40	2.1	1,283	1,283	1.00								
22-Oct-90	28-May-91	218	89			89	4.6	19,446	20,729	0.32	0.68	1991	54,775					
28-May-91	18-Oct-91	143	104			104	5.3	14,801	35,529	1.00								
18-Oct-91	29-Sep-92	347	362			362	19	125,545	161,074	0.21	0.79	1992	111,892					
29-Sep-92	14-Jun-93	258				141 **		36,399	197,472	0.36	0.64	1993	46,594					
14-Jun-93	30-Aug-93	77	6,904 *	115	193	154	7.9	11,839	209,311	1.00								
30-Aug-93	11-Jul-94	315	2,006 *	99	88	93	4.8	29,393	238,704	0.39	0.61	1994	56,229					4,287
11-Jul-94	07-Sep-94	58	415			415	21	24,047	262,752	1.00				29	6.2	1,676	1,676	
07-Sep-94	07-Jul-95	303	233	77	62	124	6.4	37,589	300,340	0.38	0.62	1995	40,513	23	4.9	6,878	8,554	10,113
07-Jul-95	12-Oct-95	97	116	103	95	105	5.4	10,143	310,483	1.00				29	6.2	2,774	11,329	
12-Oct-95	10-Jul-96	272	1,162 *	88	88	88	4.5	23,963	334,446	0.29	0.71	1996	43,172	198 *	8.3 @	10,441	65,266	19,169
10-Jul-96	29-Sep-96	81	181	93	107	127	6.5	10,290	344,736	1.00				33	7.0	2,641	67,907	
29-Sep-96	23-Jul-97	297	254		90	172	8.8	50,991	395,727	0.31	0.69	1997	39,590	98	21	29,247	97,153	21,822
23-Jul-97	09-Oct-97	78			59	59	3.0	4,565	400,293	1.00								
23-Jul-97	22-Oct-97	91			45	45	2.3	4,083	399,811	1.00				19	4.1	1,733	98,887	
	equiv. to	7.1	years			Avg =	141	(avg used for ** above)						38	(avg used in @ above)			

* High values likely due to sediment subsidence; Values not used in calculations

*** proportion of total kg of sediment collected in sed trap for a period which spanned more than one year

Table 3: Buchans 1992 Particle Samples: Granulometric Descriptions.

SITE	Total Particle Count	Particle Size Distribution as % of Total					
		<1 um	1 - 5 um	5 - 10 um	10 - 15 um	15 - 25 um	> 25 um
OWP Sed Trap	9182	22	59	10.5	5.1	2.1	1.2
OWP branch	32618	63	34	2.1	0.59	0.29	0.23
OEP branch	4081	51	42	4.1	1.4	0.59	1.1
OEP Sed Trap	20419	56	35	6.6	1.9	0.81	0.35

Table 4: Suspended Solids Concentration Distribution in OWP, 1997.

	Volume Filtered	Depth (m) Sampled	$mg.L^{-1}$ 0.1 µm	$mg.L^{-1}$ 0.2 µm	$mg.L^{-1}$ 0.45 µm	$mg.L^{-1}$ 0.8 µm
3-May-97 OWP	100 mL	5 m	0.1-1/97 -1.7	0.2-22/97 6.6	0.45-41/97 7.5	0.8-61/97 1.8
3-May-97 DT	100 mL	Surface	0.1-2/97 0.0	0.2-23/97 2.7	0.45-42/97 18	0.8-62/97 -4.6
11-Nov-97 OWP	250 mL	Surface	0.1-233/97 1.9	0.2-213/97 0.52	0.45-193/97 5.3	0.8-173/97 0.12
	250 mL	2 m	0.1-234/97 5.2	0.2-214/97 1.3	0.45-195/97 0.48	0.8-174/97 0.12
	250 mL	7 m	0.1-235/97 3.4	0.2-215/97 2.3	0.45-195/97 2.5	0.8-175/97 2.7